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USING RFID TO IDENTIFY SMART PRODUCTS ON A BLOCKCHAIN ENABLED PRODUCTION NETWORK

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ABSTRACT

Industry 4.0 requires the cooperation of several technologies. The intersections of these technologies present us with new challenges. One of these challenges is identification, since we have to identify all the items that are on the network that do work and those that are worked upon. If we fail to identify one of these items the network is presented with an unidentified potentially malicious device or a misidentified product which can cause production to halt. Blockchains or otherwise known as Distributed Ledger Technology, DLT for short is a technology that builds upon the current bookkeeping paradigm and expands it in a decentralized direction. This however can be used in more than just banking since it is essentially a distributed database that has memory of past events not just the current state. By using a blockchain based distributed database to hold processing details and using RFID-s as keys to certain entries in the database it is possible to build a tamper proof production system that can handle the challenges of industry 4.0. It may also be possible to use blockchain technology as a form of digital paper trail that can be used to validate messages sent to the nodes of the system.

Keywords: RFID, Blockchain, smart factory, smart product, data security

1. INTRODUCTION

Industry 4.0 has been labelled with many titles, one of these is Industrial Internet of Things (IIoT) [1], which is the Internet of Things (IoT) using standardised devices and achieving greater reliability. Regardless if were talking about industrial or regular IoT the main takeaway is that devices are connected on a network where they potentially can reach any other device on the network. At first glance this is a dangerous notion, since it presents an exploit also its difficult to implement since all devices need to be uniquely identifiable. According to a projection by Watanabe and Fan [2] there were to be between 26-50 billion devices connected to the internet by 2020 with no signs that the number of devices will slow their current trend. In case of fewer devices we could use IPv4, but such high numbers require IPv6 and its derivatives.

1.1. Security threats of Industry 4.0

Khan and Salah [3] place the threats in three categories depending on what level the attack is executed on. Low level attacks encompass those threats that endanger the hardware or the communications physical and data link layers. These attacks include:

- Jamming adversaries – In case of wireless communication broadcasting signals on the same frequency as required by the protocol, but the signals don't adhere to the communication protocol. (Physical layer attack)
- Insecure initialization – For a system to work properly it needs a secure initialization and setup mechanism on its physical layer, if there is none unauthorized devices can listen in on the physical layers communication.
- Low level Sybil and spoofing attacks – Sybil attacks are those attacks when an unauthorised device disguises itself as an authorised device and tries to eat up network resources. (Physical layer attack)

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- Insecure physical interface – The proper working of a device can be interfered with on physical ports such as USB or programming ports. These can be used by attackers to get access to other devices on the network (Hardware level attack)
- Sleep deprivation attack – This attack applies to devices with limited energy stores, when they need to work longer than designed for the battery will quickly drain. (Data link layer attack)

Intermediate level attacks are the attacks that use the network, transport or session layer, a few examples of such attacks:

- Replay or duplication attacks due to fragmentation – IPv6 packets need to be fragmented for devices that work according to IEEE 802.15.4, this is due to the fact that the frame size is smaller. In the case that a device receives duplicates of these packets, reassembling these consumes more than the allocated resources. This can cause buffer overflow and the reboot of the device (network layer attack).
- Insecure neighbour discovery – devices in wireless mesh networks need to discover neighbours to be able to communicate with them. Packets from an unauthorised source can lead to a denial of service attack (network level attack).
- Buffer reservation attack – a devices buffer memory that is used to assemble packets can be filled with incomplete packets, this causes a denial of service attack since the memory holding the incomplete packets is not freed (network level attack).
- RPL routing attack – the IPv6 routing protocol for Low-Powered and lossy networks (RPL) is vulnerable to several attacks from compromised devices on the network, these can deplete network resources (network level attack).
- Sinkhole and wormhole attacks – in case of sinkhole attacks the attacker responds to the routing request thereby causing the traffic to flow through the attacker node, this can be used to perform malicious activity on the network. In the case of wormhole attacks there is an tunnel through which eavesdropping, privacy violation and denial of service attacks can be executed (network level attack).
- Sybil attacks on intermediate layers – devices on the networks with false identities can initiate spamming, spreading of malware and phishing attacks (network layer attack).
- Authentication and secure communication – devices and users need to be authenticated by authenticated by key management systems. Flaws embedded in these systems house several vulnerabilities to the network (network and transport layer attack).
- Transport level end-to-end security – the purpose of this system in the transport layer is to ensure that the senders message securely arrives to the receiver (transport and network layer attack).
- Session establishment and resumption – session hijacking with forged messages can lead to denial of service attacks, also the attacker can impersonate the victim and can receive the packets meant for the victim (transport layer attack)
- Privacy violation on cloud based IoT – there are several attacks that target identity and location privacy on cloud based IoT networks. Similarly a malicious cloud service provider can access confidential information transmitted by us.

High level security issues are those that use the application layer to execute attacks, a few of these attacks are:

- CoAP security with internet – Constrained Application Protocol (CoAP) is used by devices that have very limited resources. CoAP messages follow a format described in RFC-7252 which needs to be encrypted for secure communication.
- Insecure interfaces – we can access IoT devices through the web, mobile or cloud. These interfaces are vulnerable to several attacks that target data privacy.
- Insecure software/firmware – IoT devices using SQLi and XSS languages need to be tested carefully and updates need to be carried out in a secure manner.
- Middleware security – the middleware for the heterogeneous communication of IoT devices needs to be secure enough to provide this service.

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1.2 The role of RFID in Industry 4.0

From the list of described problems we continue our exploration in the narrowed down scope to the problems within identification and secure communication, since smart products fall into this category and these are one of the innovations of Industry 4.0. Smart products are products that though directly or indirectly contain instructions for their production. By this we mean that they are identifiable and they contain information for their production either in their own memory or somewhere in a database that we can access during production. For product identification there are many solutions such as optical recognition, 1 and 2 dimensional bar codes as well as identification through RFID tags. In production systems 1 and 2 dimensional bar codes only hold information for identification all other information is stored in an external database. The advantage of this method is that a central database holds the instructions for production the product itself can't be used to inject malicious instructions also updating production instructions can be done by editing the database's corresponding entry. All foreign products can be identified if they contain an unknown bar code. However a problem arises as the identification data can be read freely since it is not encrypted, this can be circumvented as the identification data can be stored encrypted. Another problem that can arise is that products can be mislabelled with a barcode that belongs on a product with different properties that the labelled product. The advantage of barcodes is that they are cheap to produce and are not sensitive to electromagnetic noise.
RFID tags on the other hand are quite susceptible to electromagnetic noise, but carry a few advantages compared to barcodes. Firstly line of sight is not required unlike for barcodes where there is a possibility that the barcode has faded. Second RFID tags are rewritable and so can hold the instructions for production or at least part of it. The main advantage of this is that it can reduce the number of network queries but it also presents problems as well. If we believe the read data without checking that could be hazardous for it could be a destructive instruction (ex: set the temperature beyond what is required), another problem is that since the tag holds the instructions this could be read out at any time. This is bad since details of production can be stolen this way from the product itself. This brings us to the problem of mutual authentication, meaning we want to identify the device and the reader as well. Since RFID tags have limited resources any method we design has to take this into account. The problem of mutual authentication has been tackled by Sidorov et al. [4] and Mujahid et al. [5]. The proposed solutions provide protection against unauthorized reading, playback, man-in-the-middle, synchronization disrupting and tracking attacks, however the solutions proposed require 520 seconds for the communication to conclude, this area can use further improvement.
There are several case studies that present the advantages of production chains that use RFID technology [6]. These solutions require a database that houses the data required for production. In the case of a distributed database each node would have a copy of the records and the queries could be done locally. The solution we are proposing is a blockchain based system. There have been studies that explore the possibilities of using blockchains in the production system [7].

2. BLOCKCHAINS AT A GLANCE

The words blockchain and cryptocurrency propose popular new technologies, however their overabundant use might cause us to think they are nothing more than buzzwords, and cause us to miss out on this revolutionary new technology. Blockchains or Distributed Ledger Technology (DLT) is a technology that solves the problem of bookkeeping in a decentralized way, but the technology has far more uses other than bookkeeping. The currently used bookkeeping method is called double entry bookkeeping since every entry needs at least 2 pieces of data from where are we transferring and to where are we transferring to (credit and debit). This bookkeeping is done by trusted third parties such as banks or bookkeepers. However this system is not without flaws since it is human based it is prone to errors and corruption. Blockchains offer a distributed trust free alternative. It is hard to give a definitive answer when will blockchain technology become a part of everyday life, there are those that equate it to the TCP protocol

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which started out as a niche application and evolved to the backbone of the internet [8]. Currently there are 3 generations of blockchain technology.

2.1 First generation blockchains

The first generation of blockchain was proposed in a paper by Satoshi Nakamoto [9] it is currently unknown who he is and it may be possible that it is the work of a group rather than an individual. In the paper it is proposes a system where each entity that wants to do transactions has a public and a private key and all transactions are held in an open ledger. In each transaction the recipient is identified by their public key and we add a reference to the previous transaction, this information is hashed. Hashing is a mathematical function that produces a fixed length extract of the input called a hash. The hashing function has the following properties it is a one way function that is easy to compute. Meaning it is easy to calculate the hash of a given input but it is practically impossible to do the inverse of the operation (retrieve the input from the hash). The hash is used to make the entries tamper proof, since any change will produce a totally different hash. The final step in the transaction is that the sender signs the transaction with their private key as shown in Fig. 1.

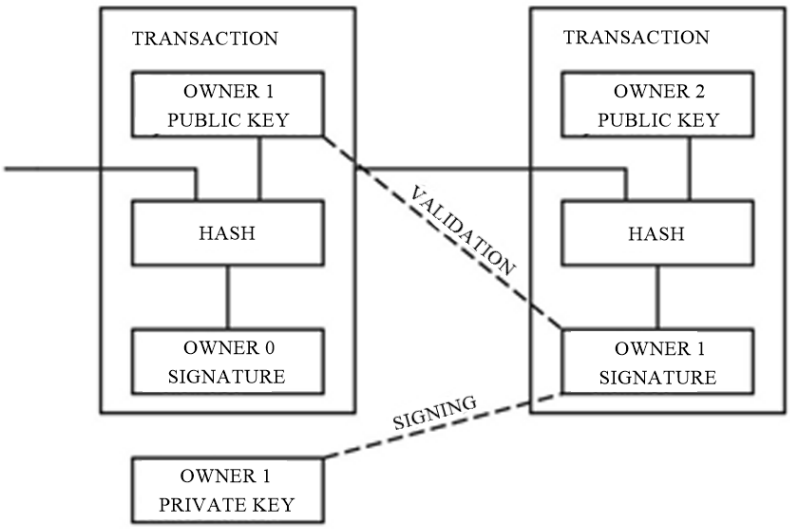

Figure 1. Transactions on a blockchain

The transactions then go to nodes called miners that place several transactions in a block, each block has the previous blocks hash and a number used only once (nonce) value as shown in Fig. 2. The miners need to figure out the value of the nonce so that the hash of the new block will start with a set number of zeroes, this is the process known as mining. Once the nonce has been calculated the node sends the newly mined block to the other nodes so they can validate the block, the process is called proof-of-work, if the block gets validated it is added to the blockchain. This proof-of-work mechanism is called a distributed systems consensus mechanism, it is a method by which the nodes can come to an agreement.

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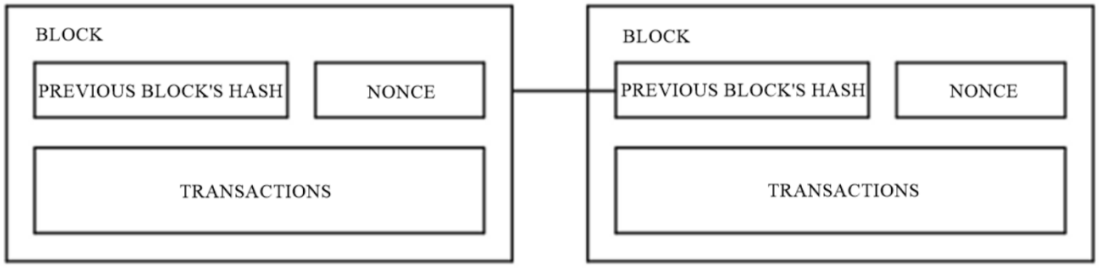

Figure 2. The structure of a blockchain

Since the only way to figure out the value of the nonce is to try all the values until there is a correct one it is computationally expensive, to reward their work the node that finds the correct nonce receives payment in cryptocurrency. The difficulty of the mining process can be adjusted up or down by adjusting the number or zeroes that are required to be in beginning of the hash, fewer zeroes easier, more zeroes increase the difficulty. Nodes follow a few simple rules on the network, they all receive all the transactions but not necessarily in the same order. Since all nodes have a copy of the blockchain they work on it can cause problems if the order of transactions is not the same for all nodes. In this case since the nonce for the blocks is correct they get attached to the blockchain and cause a fork. Since nodes always prefer the longest blockchain these forks in the blockchain die off, the transactions are logged in a different block.
Data security specifies three criteria that need to be addressed these are integrity, availability and discretion. The hashing ensures that the transactions are not altered on the blockchain. By being distributed, meaning every node has a copy of the blockchain availability is ensured. However discretion is not provided, while it is true that there is anonymity because of the public keys, the transactions cannot be denied every transaction is visible. There are so called permissioned blockchains, these unlike public blockchains don't allow anyone to read/write on the blockchain only those who are authorized. Permissioned blockchains meet all the criteria of data security. The only way to falsify an entry in a blockchain is to recalculate every nonce of every block following the one we wish to falsify this needs to be done faster than the blockchains can produce new blocks, which is really computation intensive. Such attacks are called 51% attacks, since the blockchain is constantly growing the attacker needs to have more computational power than the rest of the network to exceed the other nodes in calculating the nonce.

2.2 Second generation blockchains

The second generation of blockchains builds on the first generation by creating smart contracts [10] these are programs that are stored and executed on the blockchain. The purpose of these smart contracts is to execute when certain predefined conditions are met. The first generation two blockchain is Etherium which creates an Etherium Virtual Machine (EVM). This can be thought of as a quasi-Turing complete computer the quasi nature comes from the fact that there's maximum computational capacity which is a parameter called gas [11]. Another big difference between Etherium and Bitcoin is that the newer version of Etherium uses proof-of-stake instead of proof-of-work for a consensus mechanism where nodes do not compete with each other to find the nonce. According to the trends of the second generation we are heading for a global decentralized cloud based computer.

2.3 Third generation blockchains

The third generation of blockchains differs from the previous two by incorporating the notion of scalability, sustainability and interoperability which are major problems of the first two generations.
Blockchains have a problem with scalability, meaning that the performance of the system does not increase linearly with the number of nodes in the system. Transactions per second (TPS) in the case of Bitcoin has a

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theoretical maximum of 7 TPS and an average of 3-4 TPS. In comparison with some other money transferring systems VISA has a maximum of 56000 TPS and an average of 2000 TPS while PayPal is capable of 170 TPS [12]. The cause of this problem is the size of each block in the blockchain which has been set to 1 MB by Satoshi Nakamoto [13], a larger block size means more transactions can be processed at the same time and has the potential to drastically increase the TPS. Other cryptocurrencies experiment with greater block sizes but as of yet there is no quantifiable data. Generally it is true that the more nodes a system has the more resources are needed for its operation, since every node needs a copy of the blockchain it is not an easy thing to accomplish and may not be possible with nodes that have few resources and may not be necessary.

Another problem with first and second generation blockchains is sustainability. Nodes running the proof-of-work consensus mechanism collectively have a power consumption that rivals small countries [14]. To make the calculation of the nonce more feasible crypto-miners group themselves in mining pools where they pool their computational capacity and share in the rewards. Clumping together in pools detracts from the decentralized aspect of the blockchain since this way an attacker doesn't need to control the blockchain just the mining pool [15]. There are some alternatives to proof-of-work one of which is proof-of-stake [16]. In the case of proof-of-stake nodes do not compete with each other to be the first one to find the nonce, in this case nodes stake a specified amount of cryptocurrency the amount of which influences their chance to be chosen to validate the next block. In the case the validation is correct the staked amount plus the transaction fees are returned once the other nodes have checked the work, if it is detected that the node has cheated the staked amount is lost, this motivates honest behaviour.

The problem with interoperability is that transactions between different cryptocurrencies are difficult to achieve without a third party. The most prominent third generation blockchains are Cardano and IOTA.

3. DISCUSSION

According to Miloslavskaya the technology can be used for a secure information and event management systems (SIEM) database [17], but it has applications in other fields as well. The database built upon blockchain technology is much more resistant to traditional hacking attempts than conventional databases, once the scalability problem is solved it can be used as an un-falsifiable currency or a way to hold elections [18], or abstractly speaking the validation of past events such as the traceability of wood in the lumber industry, or validation of news sources. Smart contracts provide an excellent basis for e-governance [19]. Merging RFID and blockchain technologies is a novel idea and has seen some implementation in industry particularly the tracking of wood in the lumber industry [7]. The blockchain in this implementation provides a digital paper trail for the lifecycle of the wood and RFID is used to identify the items in question. The concept can be further built upon as the blockchain can hold more than just a paper trail for the product in question, it can also hold the next set of instructions in the production chain. Housing some or all of the instructions on the product presents an area that could be exploited by malicious actors and only serves as a means to lessen the amount of queries that need to take place on the network.

4. CONCLUSIONS

As we have presented a smart product requires two key components, a database to store the production information and a means to identify the product. RFID tags and barcodes can both be used to identify a product, however an RFID tag is more versatile and can be rewritten which is favourable. A blockchain can be used as a distributed database that has a record of past events and thus is difficult to tamper with. It satisfies the availability and integrity criteria of data security and a permissioned blockchain satisfies the discretion criteria as well. Naturally the adaptation of such a technology can expect pushback from people whose jobs it would automate, but a controlled integration is unavoidable. We can compare blockchains to email, since the advent of emails has not eliminated the post office, but made our lives easier.

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SIMULATION-BASED ANALYTICAL DESIGN FOR ALUMINIUM RECYCLING PROCESSING PLANT

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ABSTRACT

Indiscriminate disposal of beverage cans as waste poses a great threat to the environment, causing flooding, landfill, and blockage of drainages, leading to land pollution and sometimes accident. Hence, there is a need to design a system capable of converting these wastes into usable products. In this study, a simulation-based analytical design for aluminium recycling processing plant was carried out to ascertain the efficiency and reliability of the design before fabrication using finite element analysis (FEA) approach. The simulation results revealed a lesser maximum stress of 6.323 MPa for the furnace outer casing under the action of load with a displacement of 0.0795 mm. The stress of the machine components is less than the yield strength of the selected materials, making the machine fit and workable. The analytical results agree with the numerical analysis; hence the conceptual design is fit for fabrication based on the design analysis and evaluation. After the design analysis and simulation, the designed recycling process plant parts are found to be under negligible deflection and stress which is far below the yield strength of chosen materials.

Keywords. Recycling; aluminium can, ingots, conceptualization; design; simulation based.

1. INTRODUCTION

Aluminium recycling has received a tremendous attention over the years due to the remarkable benefits it offers such as drastic reduction of aluminium volume in landfills, reduction of production costs, and production of added revenue for recyclers [1-3]. However, the environment is being threatened and polluted many times due to the indiscriminate disposal of aluminium beverage cans as wastes. Hence, a recycling process is needed to convert the aluminium wastes to resources, thereby reducing the disposal of cans to the minimum hence providing permanent solution to the common problems caused by the inappropriate disposal of wastes including erosion, flooding, and drainage blockage.

Process plant has been well recognized by many engineers and producers, as an important system for combining several activities together during the manufacturing process. It is a single-unit industrial plant combining several units of machines which is often used to convert raw materials into final product of enhanced quality and properties. The process plant can reduce production time thereby reducing cost, improve the system efficiency, reduce the risks of accident to the minimum on the part of the workers, and reduce the working area or space.

Over the years, modeling and simulation approach has been used to analyze in detail the operating system and performance evaluations of many systems such as heat transfer analysis in a circular jet [4], tricycle rear shock absorber [5], network address translation (NAT)-based enterprise WLAN framework [6], denial of service (DoS) attack and defense [7], predictive analytical architecture for healthcare application [8], water distribution network [9], gate all around (GAA) FET model [10], cooperative transport [11], and shear critical glass fiber-reinforced polymer [12]. In addition, several works have been carried out on the design and analysis of different processing plants in the past. Ab Rahim et al. [13] presented an overview on recycling process of aluminium chips via hot extrusion process at the common temperature of 450°C. The ductility and strength of the Al alloy reportedly reduced as a result of deformation at high temperature. The preheat time and temperature, optimum ram speed and material

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strength were the main factors influencing the extrusion process. An extrusion process was also adopted by Patidar et al. [14] using Taughi design approach for recycling of aluminium. Recycling aluminium scraps, alloys and cans via extrusion process and other methods including hot press forging process and powder metallurgy-based method [15] often enables a simplified waste management system [16-17]. The importance of recycling process and recycled materials for several indoor and industrial applications was also emphasized by Grigore [18]. According to Kowang et al. [19], the reliability requirements, performance, cost, and safety remain the most important design criteria for recycling aluminium cans compressor. A recycling process was also carried out by Tekkaya et al. [20] on AA-6060 aluminium chips using hot profile extrusion method.

However, the conceptualization and simulation of an aluminium recycling processing plant for the production of high-grade aluminium ingots has not been properly investigated, hence the need for this study. In the present study, an aluminium recycling processing plant was conceptualized and designed to alleviate the indiscriminate disposal of beverage cans and give an eye opening on the conversion of the assumed waste to aluminium ingots. The performance of the designed process plant was then compared by analytical method and numerical approach through finite element analysis (FEA).

2. DESIGN CONSIDERATIONS AND ANALYSIS

To enhance the efficiency and reliability of the process plant without sacrificing the quality and output, some design factors were considered for the material selection and fabrication process including thermal stability, productivity time, source of power, aluminium output, safety, ease of operation, and cost [21-23].

The aluminium recycling process plant operation principle is achieved in stages and different machines are positioned to actualize this in order of operation with respect to machine in the following order; (1) can compressing machine (can crusher), (2) can shredder, and (3) electrical furnace. The electric resistance furnace is designed with the principle of a heater resistance to electric current flow leading to the production of heat. The material selected for the heater is Cr-Ni 80:20 having 20 % Chromium and 80 % Nickel. The material selection criteria for the different parts of the processing machine are summarized in Table 1.

Table 1. Material selection criteria for aluminium recycling processing plant

Machine Component	Material Selected	Selection Criteria
Can compressing machine		
Hopper volume	Mild steel	Adequate strength, cheap and readily available
Sliding piston	Mild steel	Adequate strength, cheap and readily available
Ram	304 stainless steel (SS)	Adequate strength, corrosion resistance and readily available
Fluid reservoir	304 SS	Adequate strength, corrosion resistance and readily available
Fixed end	Mild steel	Adequate strength, cheap and readily available
Machine frame	Mild steel	Adequate strength, cheap and readily available
Discharge plate	Mild steel	Adequate strength and readily available
Can shredder		
Shredder casing	Mild steel	Adequate strength, cheap and readily available
Gear	High carbon steel	High Strength, hardness, wear resistance and moderate ductility
Machine frame	Mild Steel	Adequate strength and readily available
Crusher blade	High carbon steel	High Strength, hardness, wear resistance and moderate ductility

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Gear case	S45C carbon steel	Adequate strength, corrosion resistance and readily available
Outlet channel	Mild steel	Adequate strength and readily available
Hopper	Mild steel	Adequate strength and readily available
Rotating shaft	Mild steel	Adequate strength and readily available
	Electric furnace	
Furnace outer casing	316 SS	Adequate strength, refractory, corrosion resistance and readily available
Furnace cover	316 SS	Adequate strength, refractory, corrosion resistance and readily available
Frame	Mild steel	Adequate strength, cheap and readily available
Crucible	304 SS	Adequate strength, high melting point, good conductor, corrosion resistance and readily available
Refractory	Insulating fire brick according to ASTM C155 group 23	Shrinkage less than 2% after 24hr firing at 1230^{o}C, good refractory, readily available and cheap
Heater	Nichrome 80:20	High melting point, safely heat up to 1200^{o}C

3. DESIGN ANALYSIS OF THE PROCESSING PLANT

The crushing of the aluminium cans fed to the compression hopper is pressed against a fixed wall using hydraulic principle powered by a pump, as shown in the exploded view (Figure 1) while the isometric view of process plant is shown in Figure 2. As revealed in Figure 2, the aluminium recycling processing plant comprises of the mold, furnace, conveyor, shredding and compression machine. A self-explanatory drawings and analysis are essential to uncover the operating mechanism as well as the importance of the different parts. Similar to the design analysis in literature [24-28], ease of operation and maintenance was properly considered during the design of the aluminium process plant. The can shredder consists the shredder casing, shredder hopper, crusher blade, ball bearing, outlet channel, frame, gear, electric motor and gear case.

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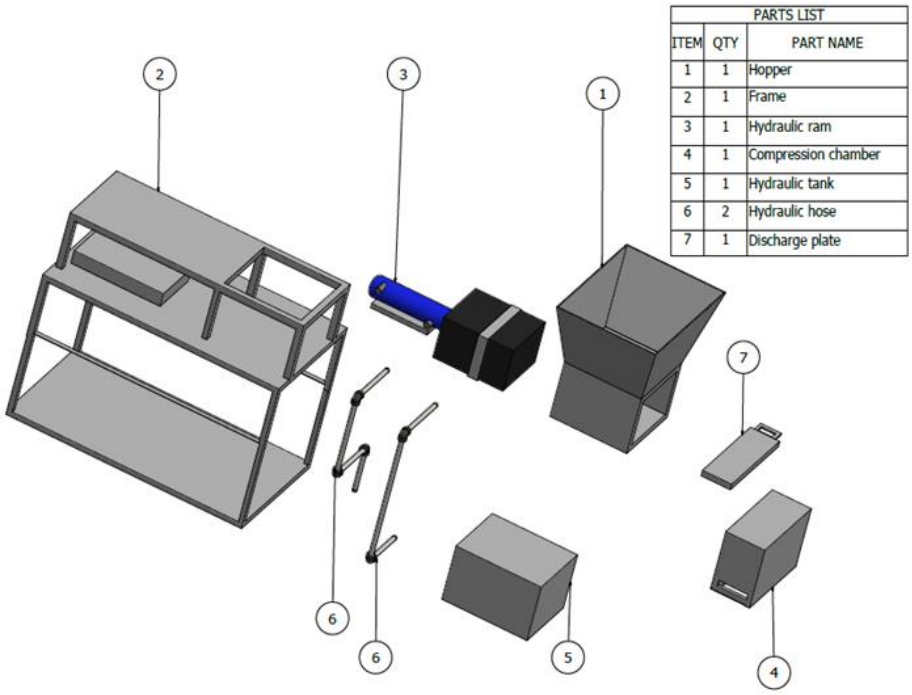

Figure 1. Exploded view of the can compression machine

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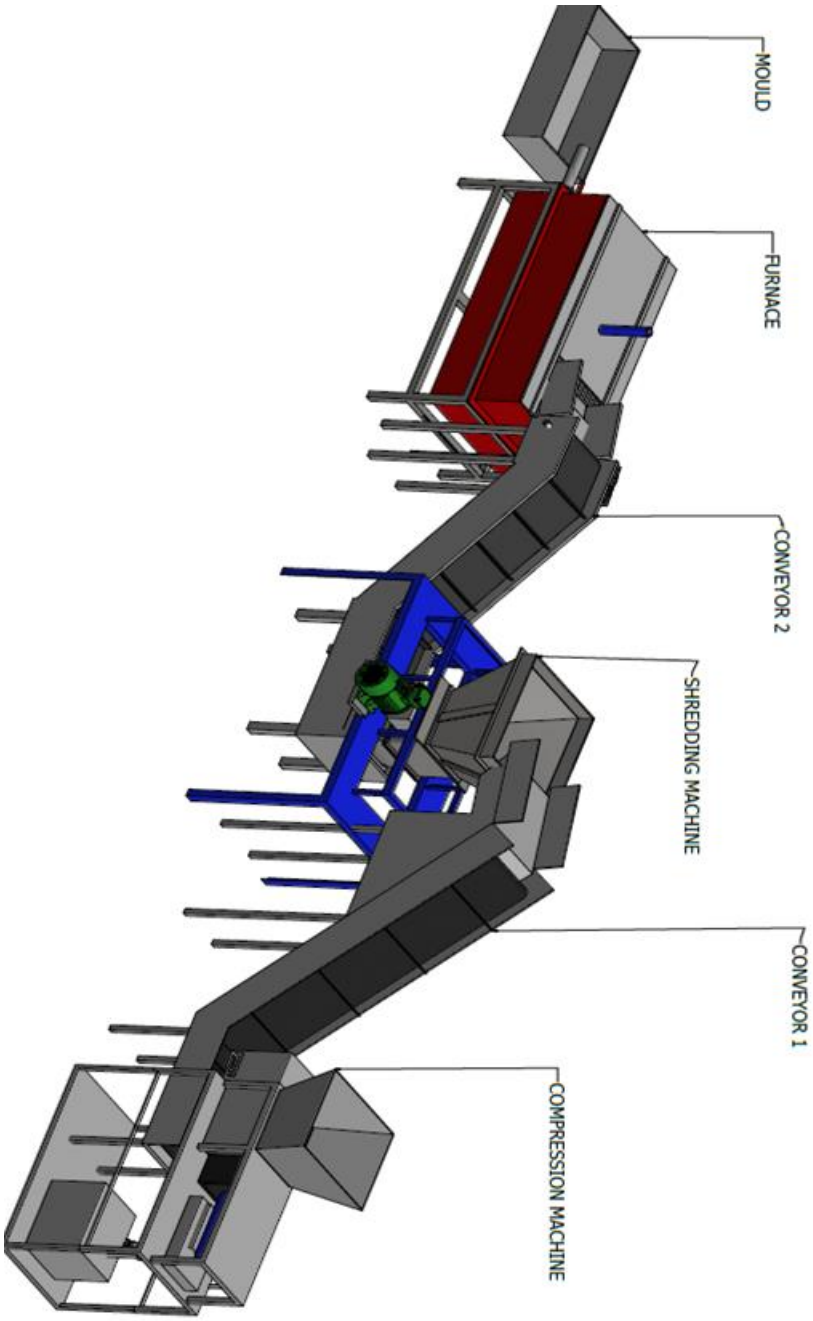

Figure 2. Isometric view of the aluminium recycling processing plant

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4. RESULT AND DISCUSSION

4.1 Analytical design of the process plant

The conceptual design of the machines has been done, and the materials selection for its production has been stated. The engineering drawings required for the production of the machine has been made available based on the design values obtained. The expected machine operation principle has been clearly stated. Table 2 - Table 6 summarize the results for the design analysis of the aluminium processing plant including the can compressing machine, cam shredder, electrical furnace, conveyor to the can shredder, and conveyor to the electrical furnace.

Table 2. Summary of design analysis for the can compressing machine part of the processing plant.

Machine Section/Part	Design Model	Design Value
Hopper volume	$V_1 = {}^1/_3(B_1H_1 - b_1h_1)$	$V_1 = 0.06983m^3$
Sliding piston	Volume, $V_0 = ((LBH) - (\pi d_1^2 L_1/4))$	$V_0 = 4.516 \text{ X } 10^{-3}m^3$
	Mass, $M_0 = \rho_p V_0$	$M_0 = 35.4506kg$
	Minimum force to move Piston, $F_m = M_o a$	$F_m = 106.3518N$
	A Stroke time = t From $(S = ut + ½(at^2)$	t = 0.408s
Ram	Volume, $V_r = ((\pi d_1^2 L_2/4) + (\pi d_1^3/16)) - ((\pi d_2^2 L_2/4) + (\pi d_2^3/16))$	$V_r = 6.016 \text{ X } 10^{-4}m^3$
Fluid reservoir	$V_{r1} = L^3$	$V_{r1} = 0.008m^3$
Minimum force needed to move piston head	Force, $F_m = M_o a$	$F_m = 106.3518N$
Hydraulic pipe	Cross sectional area, $A_p = \pi d^2/4$	$A_p = 7.854 \text{ X } 10^{-5}m^3$
	Volume flow rate, Q = Volume /time	$Q = 0.001413m^3/s$ $= 5.0868m^3/hr$
	Velocity of flow, $V_p = Q/A_p$	$V_p = 17.99m/s$
	Power through pipe, $P_n = ½ (\rho A_p v^3)$	$P_n = 193.956W$
	Workdone on fluid, $W_f = P_n$ x time	$W_f = 79.134J$
Reciprocating pump	Power, $P_p = Q\rho gH/(3.6 \text{ X } 10^6)\eta$	$P_p = 0.013425$ kW = 13.425W
Fixed end plate	Stress, $\sigma_p = F/A$	$\sigma_p = 15230.725Nm^{-2}$
Pump	Power, $P_p = \frac{Q.P}{\eta}$	320.07 W 1hp hydraulic actuator pump is selected

Table 3. Summary of design analysis for the can shredder part of the processing plant.

Machine Section/Part	Design Model	Design Value
Hopper volume	$V_2 = {}^1/_3(B_2H_2 - b_2h_2)$	$V_2 = 0.173733m^3$
Shaft 1 and 2	Volume (V_0) = ((πd^2)/4) *L	$V_0 = 7.5398 \text{ X } 10^{-4}$ m^3
Shaft 1and 2	Mass (M_0) = M_0 X ρ	M_0 = 5.9187kg
Shaft 1 and 2 velocity	$V = \frac{2\pi N}{60}.\frac{d}{2}$	V = 0.2094 m/s
Turning force if shaft 1 and 2	$F_t = \frac{2M_oV^2}{d}$	$F_t = 12.98\ N$
Torque of shaft (T)	$\frac{T}{J} = \frac{\tau}{d/2}$	$T = 565486.7$ Nmm = 565.4867 Nm
Shaft angle of twist (Θ)	$\frac{\tau}{d/2} = \frac{T}{J} = \frac{C.\theta}{L}$	0.01687 rad = 0.96658^0
Power needed to rotate shaft (P)	$P = T\omega = \frac{2\pi NT}{60}$	$P = 5921.763\ W$ = 5.922 kW
Maximum shear strain in the shaft $(e_s)_{max}$	$(e_s)_{max} = \frac{\frac{d}{2}.\theta}{L}$	$5.62\ X\ 10^{-4}$
Torsional rigidity (k)	$k = \frac{T}{\theta}$	33520.0255 Nm/rad
Bending moment of shaft 1	B.M = (WL/2)/2 = WL/4	B.M = 8700.495Nmm
Shaft 1 angle of deflection	$\theta_{max} = \frac{-WL^2}{EI.16}$	Θ_{max} = -0.002975^o
Shaft 1 deflection	$y = \frac{-WL^3}{48EI}$	$y = -1.0386\ X\ 10^{-5}\ m$ = -1.0386 X 10^{-5}m ≈
Shaft 2 angle of deflection	$\theta_B = \frac{-WL^2}{2EI}$	θ_B =-4.1543 X 10^{-4} rad = -0.0238^0
Possible maximum deflection (y_{max}) that could occur in shaft 2	$y_{max} = \frac{-W}{EI}\left(L.\frac{L^2}{2} - \frac{L^3}{6}\right) = \frac{-WL^3}{3EI}$	y_{max} = 0.00016617 m ≈ 0.166 mm
Gear circular pitch	P_c = Circular pitch = πm	$P_c = 3\pi = 9.4247 \equiv 9.425$mm
Center distance between pitch circle	X = Center distance between pitch circle = $\frac{D_1+D_2}{2}$	X = 60mm
Pitch line velocity	$v = Pitch\ line\ velocity = \frac{\pi DN}{60}$	V = 0.6283m/s
Velocity factor	$C_v = \frac{3}{3+v}$	C_v = 0.8268
Permissible working stress	$\sigma_w = \sigma_o$ X C_v	$\sigma_w = 57.876Nmm^{-2}$
Tangential load on a tooth	$W_T = \sigma_w.b.\pi m.y$	W_T = 1959.32 N

Table 4. Summary of design analysis for the electrical furnace part of the processing plant.

Machine Section/Part	Design Model	Design Value
Volume of crucible	V_3 = LBH	$V_3 = 945000000mm^3$ = $0.945m^3$

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Limited volume of crucible to be used	V_4 = 80% of V_3	= 0.756m^3
Mass of molten aluminium of 756km^3 volume (m_1)	m_1 = Density of molten aluminium X 0.756m^3	m_1 = 1795.5kg
Quantity of heat needed to melt aluminium and raise it to 700^oC (Q_T)	$Q_T = m_1C_{Al}((T_2 - T_1) + (T_3 - T_2)) + m_1L_{Al}$	1811659500J = 1.812 X GJ
Total thermal conduction resistance	$R_{th.con} = \frac{(0.03k_f + L_f k_s)}{k_s k_f} X \left(\frac{1}{A_1} + \frac{1}{A_2} + \frac{1}{A_3} + \frac{1}{A_4} + \frac{1}{A_5} + \frac{1}{A_6}\right)$	$R_{th.con}$ = 0.58917 $m^2/s\ ^0K/$ kJ
Heat loss to crucible (absorbed)	Heat use for raising material to 800 ^oC = m_sC_{st} (800 - 20)	1400 X 502.416 X 780 = 548638272 J
Total heat to be produced (Q_t)	= Heat for melting Aluminium + Heat loss by conduction + Heat lost to crucible	2361451938 J ≈ 2.361 GJ
Furnace Efficiency (η_f)	$\eta_f = \frac{useful\ heat}{total\ heat}$	76.72%
Time needed to melt filled aluminium (T)	$T = \frac{Q_t}{I.V.(60\ X\ 60)}$	7.809 hours ≈ 8 hours

Table 5. Summary of design analysis for the conveyor delivering to can shredder part of the processing plant.

Machine Section/Part	Design Model	Design Value
Length (L5)	L5 = $\sqrt{h^2 + l^2}$	$L5$ =1.281 m
Mass of belt	$\rho_{b.}L.b_{o.}w$	141.3L kg
Belt weight	$W_b = \frac{m_b}{L}.9.81$	$1386.153\frac{kg}{m}$
Number of carrying idlers for L6	$t_c = \frac{L6}{Z_{c6} + 1}$	Z_{c6} = 19.3443 ≈ 19 idlers
Number of carrying idlers for L3	$t_c = \frac{L3}{Z_{3c} + 1}$	Z_{3c} = 7.33 ≈ 7 idlers
Number of return idlers for L1	$t_r = \frac{L1}{Z_{r1} + 1}$	Z_{c5} = 7.33 ≈ 7 idlers
Number of return idlers for L2	$t_r = \frac{L2}{Z_{r2} + 1}$	Z_{c5} = 10.667 ≈ 11 idlers
Possible number of compressed cans	$n_c = \frac{1.72}{0.2094\ X\ 0.408}$	.= 20.13 = ≈ 20

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Mass per unit meter of aluminium conveyed	$m_m = \frac{216.66}{1.72}$	$= 125.97 kg/m$
Load resistance due to lifting of material (F_f)	$F_f = W_m \cos\theta = m_m . L . g . \cos\theta$	$F_f = 1076.073\ N$
Component of load along belt	$F_m = W_m \sin\theta = m_m . L . g . \sin\theta = m_m . g . h$	$F_m = 865.0356\ N$
Frictional resistance due to carrying idlers F_{cr}	$F_{cr} = F_c \left(m_m + m_b + \frac{m_i z_c}{l}\right) gl$	F_{cr} = 113.9044 N
Frictional resistance due to return idlers F_r	$F_r = F_c \left(m_b + \frac{m_i z_r}{l}\right) gl$	F_{cr} = 75.5012 N
Minimum diameter of conveyor driver drum	$d_A = \frac{f_u . C_3 . 180}{b_0 . \beta}$	$d_A = 60.38\ mm \approx 60\ mm = 0.06m$

Table 6. Summary of design analysis for the conveyor delivering to electrical furnace part of the processing plant.

Machine Section/Part	Design Model	Design Value
Belt weight	$W_b = \frac{m_b}{L} . 9.81$	$1386.153 \frac{kg}{m}$
Number of carrying idlers for L6	$t_c = \frac{L6}{Z_{c6} + 1}$	Z_{c6} = 4.833 ≈ 5 idlers
Number of carrying idlers for L5	$t_c = \frac{L5}{Z_{5c} + 1}$	Z_{c5} = 20.35 ≈ 20 idlers
Number of return idlers for L4	$t_c = \frac{L4}{Z_{c4} + 1}$	Z_{c5} = 10.66 ≈ 11 idlers
Number of return idlers for L1	$t_r = \frac{L1}{Z_{r1} + 1}$	Z_{r1} = 3.16 ≈ 3 idlers
Number of return idlers for L2	$t_r = \frac{L2}{Z_{r2} + 1}$	Z_{r2} = 8.667 ≈ 9 idlers
Possible number of crushed to block cans (N_o)	$N_o = \frac{Volume\ of\ compressed\ cans}{volume\ of\ shredder\ hopper}$	50.6 ≈ 51
Load resistance due to lifting of material (F_f)	$F_f = W_m \cos\theta$ $.= m_m . L . g . \cos\theta$	$F_f = 2855.312\ N$
Component of load along belt	$F_m = W_m \sin\theta = m_m . L . g . \sin\theta = m_m . g . h$	$F_m = 3596.43\ N$
Frictional resistance due to carrying idlers F_{cr}	$F_{cr} = F_c \left(m_m + m_b + \frac{m_i z_c}{l}\right) gl$	298.0877 N
Frictional resistance due to return idlers F_r	$F_r = F_c \left(m_b + \frac{m_i z_r}{l}\right) gl$	127.1003 N

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Minimum diameter of conveyor driver drum	$d_A = \frac{f_u . C_3 . 180}{b_0 . \beta}$	$d_A = 192.63\ mm \approx 200\ mm = 0.2m$
Velocity of drum drive and belt speed (V)	$V = \frac{\pi d_A N}{60}$	$V = 0.2094\ m/s$
Electric motor power (P_m)	$P_m = \frac{P_A}{\eta}$	P_m = 1498.185 W ≈ 1.498 kW ≈ 1.5 hp

4.2 Simulation-based design

The simulation was done using Autodesk inventor software and the results are analyzed. Figure 3 shows the simulation of the furnace frame; with the simulation displacement result of furnace frame when loaded shown in Figure 3(a), furnace frame simulation Von Mises stress result in Figure 3(b), and furnace frame stress XY simulation result in Figure 3(c). From the result simulation result of the electrical furnace frame, a maximum stress of 55.91 MPa which is lesser than the yield strength (207 MPa) of the material, can be experienced by the frame. In addition, the displacement experienced by the electrical furnace frame due to the applied force and pressure, can be up to 1.023 mm. The displacement is very negligible, having no effect on the component, hence no failure of part under operation. Figures 3(d-f) show the simulation of can compressing machine frame. As revealed in Figure 3(d), the maximum stress experienced by the frame is 3.12853 MPa. The displacement experienced by the can compressing machine frame due to the applied force and pressure is 0.02018 mm, as shown in Figure 3(e) and summarized in Figure 3(f).

The result obtained from the simulation of the can compressing machine piston head (Figures 3(g-i)) shows that the maximum stress experienced by the frame which can be as high as 0.27179 MPa (Figure 3(g)). Due to the applied force and pressure, the displacement experienced by the can compressing machine piston head can be up to 0.00025654 mm, as revealed in Figures 3(h-i).

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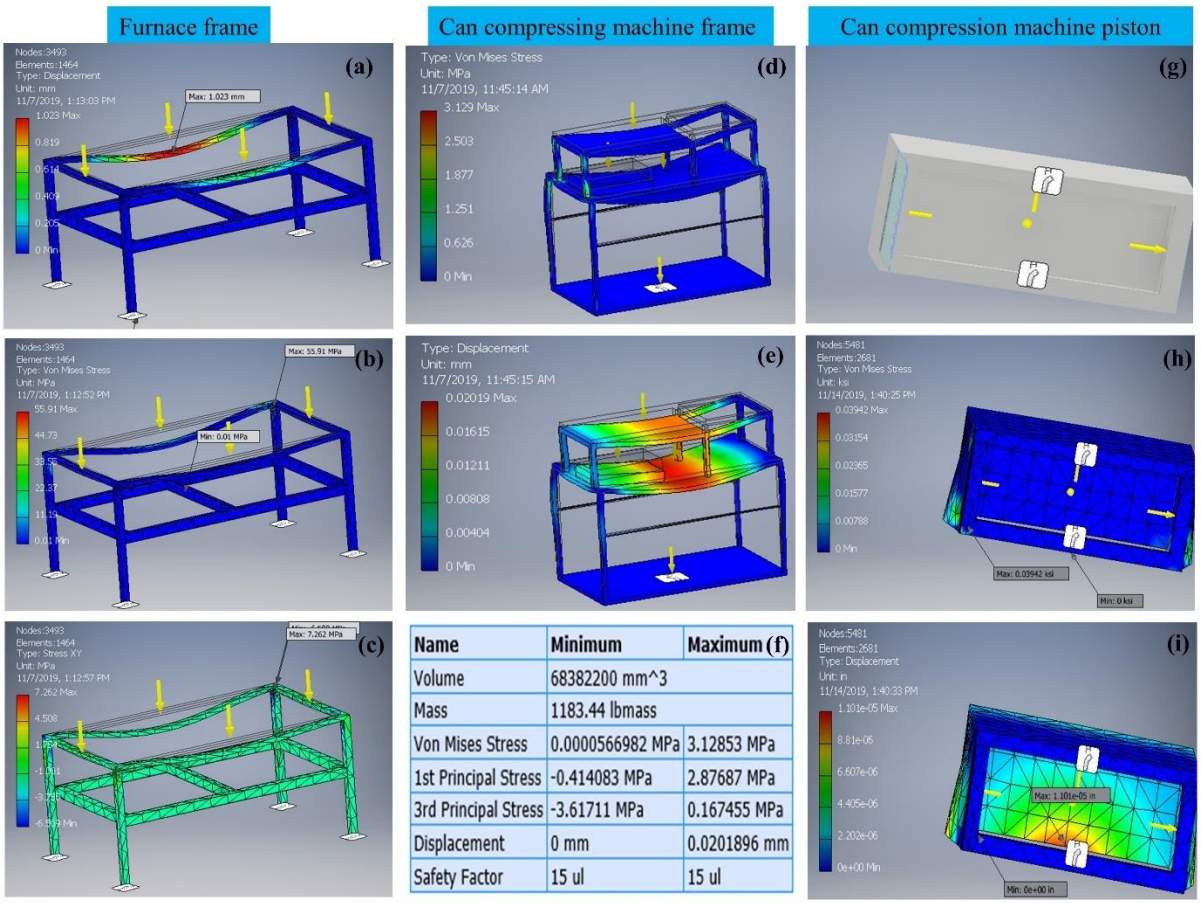

Name	Minimum	Maximum (f)
Volume	68382200 mm^3	
Mass	1183.44 lbmass	
Von Mises Stress	0.0000566982 MPa	3.12853 MPa
1st Principal Stress	-0.414083 MPa	2.87687 MPa
3rd Principal Stress	-3.61711 MPa	0.167455 MPa
Displacement	0 mm	0.0201896 mm
Safety Factor	15 ul	15 ul

Figure 3. Simulation of the furnace frame, can compressing machine frame, and can compression machine piston head; (a) simulation displacement result of furnace frame when loaded, (b) furnace frame simulation Von Mises stress result, (c) furnace frame stress XY simulation result, (d) can compressing machine frame Von Mises stress simulation result, (e) can compressing machine frame displacement result of simulation, (f) summary of the can compressing machine simulation result, (g) can compressing machine piston head at no load, (h) Von Mises stress result of can compressing machine piston head, (i) displacement result of piston head.

Figure 4 shows the simulation results for the can shredder gear, can shredder base cover, and electrical furnace refractory cover. Figure 4(a) shows the result obtained from the simulation of the can shredder gear tooth revealing the maximum stress experienced by the frame to be 7.559 MPa. From Figure 4(b), a displacement of 0.00001 mm can be obtained for the can shredder gear tooth due to the applied force and pressure. Figure 4(c) reveals the Von Mises stress simulation result showing a tooth on gear.

Figure 4(d) shows the result obtained from the simulation of the label removal machine frame revealing the maximum stress experienced by the frame to be 4.293 MPa. In addition, a very small displacement of about 0.005357 mm (Figure 4(e)) can be experienced by the label removal machine frame due to the applied force and pressure. The negligible displacement obtained indicates that the component cannot be affected and hence no failure will occur under operation. This is also confirmed by the displacement simulation result on can shredder base, as revealed in Figure 4(f).

Figure 4(g) shows the simulation results of the electrical furnace refractory with the maximum stress of 6.323 MPa for the frame. The subsequent displacement obtained for the electrical furnace refractory is 0.07954 mm (Figure

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4(h)), which can be attributed to the effect of the applied force and pressure. The displacement of the electrical furnace refractory cover simulation result showing the base is revealed in Figure 4(i). Table 7 summarizes the simulation results for the processing plants.

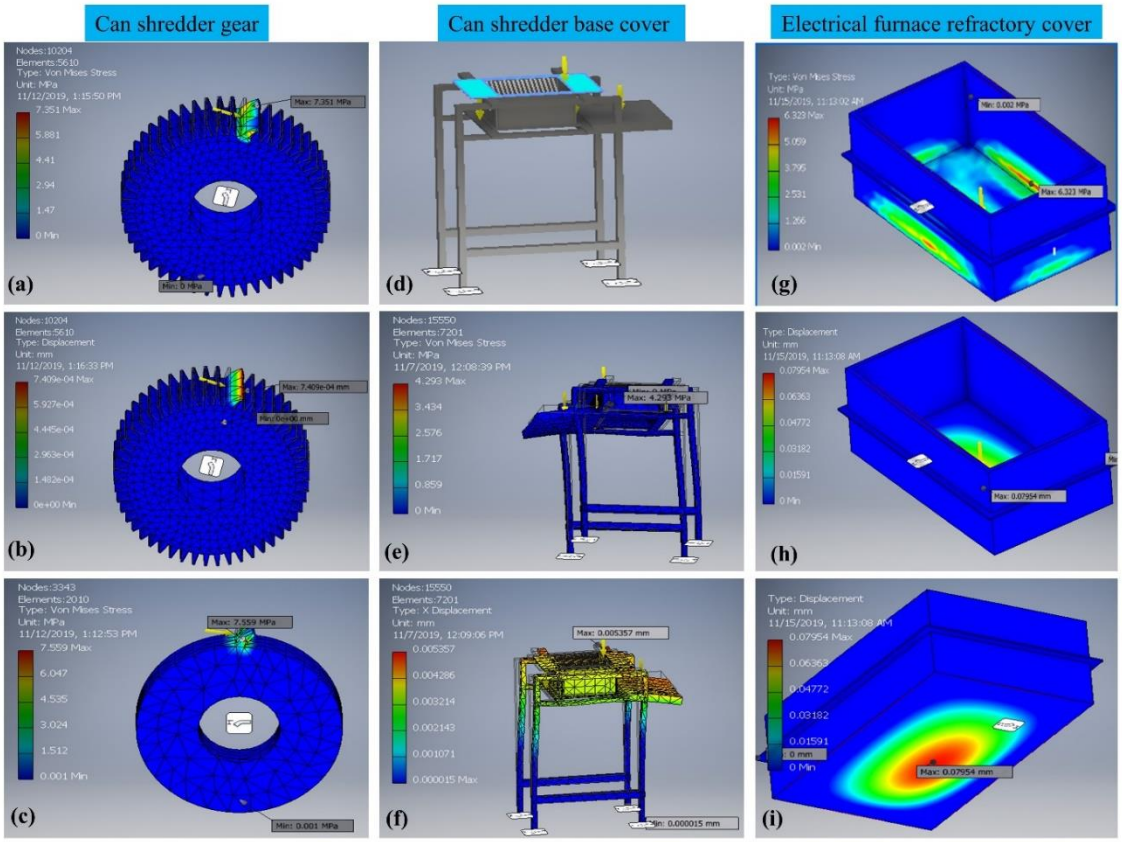

Figure 4. Simulation of can shredder gear; (a) Von Mises stress simulation result on a gear tooth, (b) displacement result on the gear tooth, (c) Von Mises stress simulation result showing a tooth on gear; simulation of can shredder base cover: (d) can shredder base with frame at no load, (e) Von Mises stress simulation result on can shredder base with frame, (f) displacement simulation result on can shredder base; electrical furnace refractory cover: (g) Von Mises electrical refractory cover stress simulation result, (h) displacement of electrical refractory cover simulation result, (i) displacement of electrical furnace refractory cover simulation result showing base.

In this study, the stress of the machine components is less than the yield strength, making the machine fit and workable. In addition, as revealed in Table 7, the analytical and simulation results agree with each other, hence the conceptual design is fit for fabrication based on the design analysis and evaluation, using the available materials.

Table 7. Comparison of results (maximum stress) for both analytical method and numerical simulation

Parts	Analytical method (MPa)	Numerical method (MPa)
Electrical furnace frame	56.902	55.910
Can compressing machine Frame	3.500	3.128

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Can compression machine piston head	0.310	0.272
Can shredder gear	7.920	7.559
Can shredder base cover	4.523	4.293
Electrical furnace refractory cover	6.632	6.323

Simulation-based approach is not only core to recycling and resource efficiency, but also validate and evaluate the performance of analytical model which makes it to be an important tool in many applications including anti-synchronization of non-identical hyperchaotic systems [29], double circuit transmission system [30], indoor temperature control [31], traffic flow variables at network [32], etc. In the present study, the simulation-based designed process plant will find applications in many beverage manufacturing industries for the production of high-quality aluminium ingots through recycling, hence reducing the amount of wastes to the minimum [33].

5. CONCLUSIONS

In summary, a simulation-based analytical design for aluminium recycling processing plant was carried out for the production of high-grade aluminium ingots. The plant was designed to have a compression section, a shredding section, a furnace where melting process is achieved, and conveyors positioned between sections. The design analysis of each of the machine element was done and structural integrity of the machine design was evaluated using finite element modeling. The simulation results revealed a lesser maximum stress of 6.323 MPa for the furnace outer casing under the action of load with a displacement of 0.0795 mm, whereas the analytical method yielded a maximum stress of 6.632 MPa. Regarding the electrical furnace frame, the maximum stress of 56.902 MPa and 55.910 MPa were obtained for the analytical and numerical methods, respectively. The stress of the machine components is less than the yield strength, making the machine fit and workable. The analytical and simulation results agree with each other; hence the conceptual design is fit for fabrication based on the design analysis and evaluation, using the available materials. The developed aluminium recycling processing plant will find applications in many beverage manufacturing industries for the production of high-quality ingots.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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EFFECT OF DIFFERENT DRYING TECHNIQUES ON THE DRYING TIME AND ENERGY OF BLUEBERRY

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ABSTRACT

Blueberries (*Vaccinium corymbosum* L.) were dried combining vacuum, infrared, hot-air and freeze drying technologies. In this paper, examined the drying time and energy consumption of dewatering methods. The rehydration as a physical property were evaluated in dried blueberries. Combination of vacuum dried and freeze dried blueberries had higher rehydration ratio, followed by the single freeze drying, combination of hot-air drying and freeze drying, and infrared-freeze drying methods. The performance evaluation indicated that combination drying of blueberries at two-stage infrared-freeze drying with 60°C and 15 min pre-drying reduced the drying time by 53.4%, besides consuming less energy (52.9%) compared to single freeze drying. Based on the results, primarily vacuum pre-drying, infrared pre-drying and freeze finish-drying may be the economical and optimal solution for dehydrating blueberries.

Keywords: single- and two-stage drying, drying time, energy uptake, rehydration, blueberry

1. INTRODUCTION

The consumers are gradually interested in the health benefits of foods and have begun to look beyond the basic nutritional benefits to the potential illness prevention and health enhancing compounds contained in many foods. Fruits and vegetables are natural sources of healthy bioactive compounds and mineral nutrients, exhibiting significant health benefits [1]. Blueberries (*Vaccinium corymbosum* L.) have become very popular with purchaser because of the research results that associate their consumption with improvements in human health [2]. Nowadays, blueberry intake is of high interest due to its high content of antioxidant compounds (flavonoids and anthocyanins) and vitamin A, B, C and E. Blueberries are well known for their anticancer, anti-inflammatory and antidiabetic properties [3].

Drying of fruit and vegetables is one of the most common processes used to improve the stability, as it reduces the water activity of product, cut down on microbiological activity, reduces in weight and volume and minimizes physical and chemical changes during storage [4].

Nowadays, drying of fruits and vegetables principally accomplishing by hot-air drying (HAD). The high temperature of the drying method is an important cause of loss of chemical compounds and change in appearance. Some important physical properties of the final products are changed by this dewatering technique such as loss of color, change of texture, shrinkage, chemical changes affecting flavour and nutrients [5].

The infrared drying (IRD) occurs by the exposure of the raw matter to electromagnetic radiation. The infrared radiation energy is transferred from the heating element to the material surface. However, the surrounded air is not heated in the drying process [6]. Compared with HAD, the IRD heating offers many advantages such as greater energy efficiency, heat transfer rate, which results in decreased operational time and higher drying rate [7].

The vacuum drying (VD) is a remarkable procedure for heat sensitive substances. Under atmospheric pressure drying can be considered according to physical state used to add heat and remove water vapour. Low temperature can be used under vacuum for certain techniques that might discolour or degrades at high temperature [8].

Higher quality products can be obtained using more expensive freeze-drying (FD) process. The solid state of water during FD protects the structure and minimizes changes in the form of the final product, with

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minimal shrinkage [9]. In addition, it contributes to preserve mineral nutrients and vitamins, as well as to retain original aroma and flavour [10].
Energy and working time efficiency are one of the most important design and operational parameters in food processing, so the importance of combined drying has increased. Combined, two-stage drying, or otherwise tandem drying, is a drying solution where one drying method is followed by another drying process. There are many combinations of drying techniques. Target to avoid the disadvantages of the single drying method, e.g. the long drying time, high energy consumption or unfavourable product quality [11].
No one has reported on the two-stage drying (HAD-FD, IRD-FD and VD-FD) of blueberries. The aim of the present study is to determine the combined drying program and to evaluate the effect of single- and two-stage drying on drying time, energy consumption, and rehydration.

2. MATERIALS AND METHODS

2.1. Materials

The blueberries were purchased from a local supermarket in Nyiregyhaza, Hungary. Before the experiments, initially the blueberry fruits were thoroughly washed. Before freeze drying the samples pre-treated with quick-freezing (T=- 25°C) in quick freezer (FT34MKII, Armfield Ltd., Ringwood, England).
The average diameter of a blueberry was 1 cm ± 0.2 cm. The samples were divided into thirteen groups, each group of samples weighed 100 g. Moisture contents of raw and dried blueberry samples was measured by the gravimetric method using a laboratory convection oven (model LP302, LaborMIM, Budapest, Hungary) at 105 ± 1 °C until a constant weight was reached. Average moisture content of fresh blueberry was 88.1% in wet basis. The samples were dehydrated until they reached the final moisture content (2-3% w.b.).

2.2. Methods

The hot-air drying (HAD) was realized in a cabinet drier (model LP305, LaborMIM, Budapest, Hungary). The drying temperature was fixed at 60°C. According to the previous literature, the optimum drying conditions of hot air drying for foods were 60°C hot air temperature [12, 13]. The weight of sample was measured (model JKH-500, Jadever Co., New Taipei, Taiwan), every 60 minutes, for a total duration of seven hours. A suitable blower was fitted for air circulation in the drying chamber which is leading to an air velocity of 1 m/s over the trays. The samples were placed in one layer on the sample holder.
A laboratory scale vacuum dryer (VD) was used for vacuum dehydration of the samples (model Kambic VS-50C, Kambic Lab. Eq., Semic, Slovenia). The vacuum pump provides pressure in the chamber 5000 Pa under the drying. The temperature in the chamber was set at 60°C for each treatment. Temperatures of the samples were monitored using type T thermocouples throughout the experiment. Blueberry mass was recorded with balance (model JKH-500) every 1 hours, which has a sensitivity of 0.1 g. The samples were uniformly spread in single layer on the tray.
Infrared drying (IRD) was performed in a laboratory digital infrared dryer (model Precisa HA60, Precisa Instruments AG, Dietikon, Switzerland). Two infrared heaters were operated at 230 V with a maximum power of 410 W. The sample tray was kept 15 cm below the infrared heater throughout the experiment. The drying air temperature was kept at 60°C, which is corresponds to a heat intensity level of 4.5 kW/m^2. The mass of the blueberry was measured using a digital electronic balance (model Precisa HA60) at intervals of 5 min during the drying experiment. Each 100 g samples were uniformly spread in single layer on a stainless steel tray.
Freeze drying (FD) was performed using a lab scale freeze dryer (model Christ Alpha 1-4 LSC Plus, Martin Christ GmbH, Osterode am Harz, Germany) (Fig. 1.). Heating shelf temperature was set at 20°C, and the cold trap temperature was maintained at -45°C. Samples temperatures were measured by the T-type thermocouples inserted into the samples. During drying, 100 g of samples were dehydrated in the chamber with an internal pressure of 50 Pa produced by the vacuum pump. The samples were uniformly spread in single layer on the tray.

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Figure 1. Christ Alpha 1-4 LSC Plus laboratory vacuum freeze dryer with blueberry samples

The drying parameters of each drying conditions was listed in Tab. 1.

Table 1. Description of the drying programs

No	Acronym	Description	Air		Power	Pressure
			T (°C)	v (m/s)	(kW/m^2)	(Pa)
1	HAD	Single-stage Hot-air drying	60	1	-	10^5
2	IRD	Single-stage Infrared drying	60	-	4.5	10^5
3	VD	Single-stage Vacuum drying	60	-	-	5^3
4	FD	Single-stage Freeze drying	-20 - +20	-	-	50
5	HAD2-FD	Combined hot-air freeze drying	60; -20 - +20	1	-	10^5→50
6	HAD3-FD	Combined hot-air freeze drying	60; -20 - +20	1	-	10^5→50
7	HAD4-FD	Combined hot-air freeze drying	60; -20 - +20	1	-	10^5→50
8	IRD5-FD	Combined infrared freeze drying	60; -20 - +20	-	4.5	10^5→50
9	IRD10-FD	Combined infrared freeze drying	60; -20 - +20	-	4.5	10^5→50
10	IRD15-FD	Combined infrared freeze drying	60; -20 - +20	-	4.5	10^5→50
11	VD2-FD	Combined vacuum d. freeze drying	60; -20 - +20	-	-	5^3→50
12	VD3-FD	Combined vacuum d. freeze drying	60; -20 - +20	-	-	5^3→50
13	VD4-FD	Combined vacuum d. freeze drying	60; -20 - +20	-	-	5^3→50

The dried blueberry samples were packed immediately into PE bags after drying for further analyses. Combined or two-stage drying procedure: Experiments were performed using combined drying methods until the final sample moisture content. The settings for each stage are given in Tab. 2.

Table 2. Description of drying treatment combinations

No	Acronym	First drying stage (m. c. in w.b.)	Second drying stage (m. c. in w.b.)
1	HAD2-FD	60°C for 2h until the moisture c. was 54.5%	20°C until the moisture c. below 2.6%
2	HAD3-FD	60°C for 3h until the moisture c. was 40.3%	20°C until the moisture c. below 2.4%
3	HAD4-FD	60°C for 4h until the moisture c. was 33.7%	20°C until the moisture c. below 2.9%
4	IRD5-FD	60°C for 5 min until the moisture c. was 46.9%	20°C until the moisture c. below 2.1%
5	IRD10-FD	60°C for 10 min until the moisture c. was 35.4%	20°C until the moisture c. below 2.2%
6	IRD15-FD	60°C for 15 min until the moisture c. was 26.5%	20°C until the moisture c. below 2.6%
7	VD2-FD	60°C for 2h until the moisture c. was 59.2%	20°C until the moisture c. below 3.0%
8	VD3-FD	60°C for 3h until the moisture c. was 44.4%	20°C until the moisture c. below 2.7%
9	VD4-FD	60°C for 4h until the moisture c. was 36.2%	20°C until the moisture c. below 2.8%

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The specific energy consumption during dehydration was measured by an energy-cost-checker (model EKM 265, Conrad Electronic GmbH, Hirschau, Germany), and the energy consumption required to remove 1 kg of water was calculated. The specific energy consumption (SEC) in MJ/kg_{water} was estimated as follows (1):

$$SEC = \frac{E \times 3,6}{W_0 - W_f}, \quad (1)$$

where E is the electrical power consumption [kWh], W_0 is the initial mass of the raw material [kg], W_f is the final mass of the dried sample [kg].

Description of rehydration procedure: The dried samples were soaked in 30°C± 1°C distilled water for 1 h, then the free water on the surface of the samples was removed with a filter paper. The rehydrated samples weighed with an electronic digital balance having a sensitivity of 0.01 g. The rehydration ratio (RR) was calculated according to Eq. (2):

$$RR = \frac{W_r}{W_d}, \quad (2)$$

where W_r is the drained weight of the rehydrated sample [g], W_d is the weight of the dry sample used for rehydration [g].

Statistical analysis was conducted by analysis of variance (ANOVA) using Duncan's test to detect the differences among drying methods (SPSS 20.0, IBM Inc., USA). All drying condition were replicated three times.

3. RESULTS AND DISCUSSION

3.1. Drying time

The Fig. 2 shows the significant effect ($p<0.05$) of different drying techniques on the drying time. Drying (initial moisture content, 88.1% w.b.) continued until the final moisture content was ca. 2-3% (w.b.). It is observed that the drying time for HAD, IRD, VD, FD, HAD2-FD, HAD3-FD, HAD4-FD, IRD5-FD, IRD10-FD, IRD15-FD, VD2-FD, VD3-FD and VD4-FD was 420, 75, 480, 1320, 1080, 960, 900, 785, 670, 615, 1140, 960 and 900 minutes, respectively.

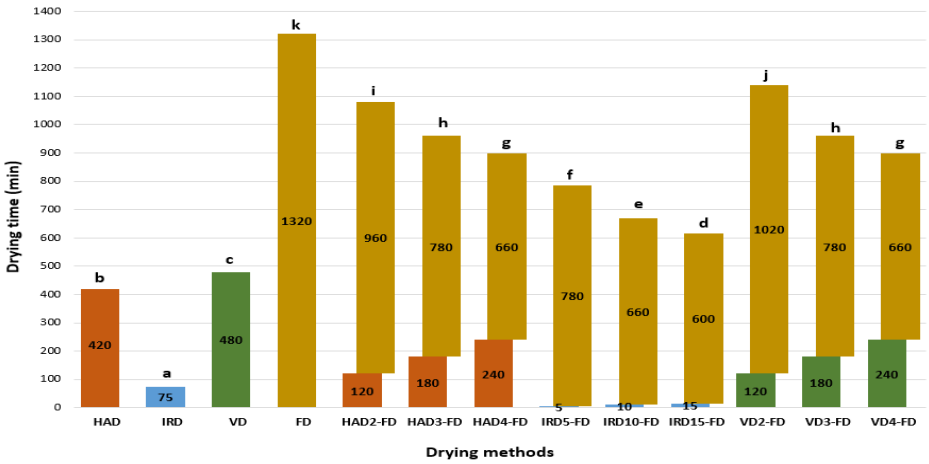

Figure 2. Results of drying time of dried blueberry samples under different drying techniques
Bars with different letters differ significantly from each other as determined by Duncan's test.

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Lyophilization (FD=22h) has the longest treatment time at blueberry, in agreement with previous studies [14, 15]. Pre-freezing of the blueberry sample has a good effect on the operating time of lyophilization as it reduced the drying time from 26 to 22 hours. Compared to FD, the IRD15-FD significantly ($p<0.05$) reduced drying time by 53.4%.

For the combined drying methods, the pre- and finish-drying are marked with different colours. Fig. 2 shows that the drying time in the IRD-FD method (785, 670 and 615 min) was the shortest among hybrid drying techniques. Reyes et al. [16] dried the blueberries in a freeze dryer equipped with a 150 W infrared halogen lamp. It was found that the IRD application accelerated the drying process. The operating time of freeze-drying was reduced to 12 hours with this solution. In particular, the drying time required for dehydration with IRD15-FD to reach a moisture content of 2.6% (w.b.) was 1.46 times less than HAD4-FD and VD4-FD methods, respectively. The increase in heat intensity level at IRD might have caused a rapid rise in the temperature at surface of product, resulting into an increase in the water vapour pressure inside the material and thus in higher drying rates [17].

It was found, that the drying time decreased significantly ($p<0.05$) with increased a pre-drying time (2-3-4 h and 5-10-15 min) under a constant drying temperature (60°C) and infrared power (4.5 kW/m^2). Furthermore, it was found that 5 hours of pre-drying for VD and HAD and 20 minutes of pre-drying for IRD cause a noticeable browning (so called Maillard reaction) on the surface of the products, so the results of these settings are not reported.

3.2. Specific energy consumption (SEC)

Effect of single and two-stage drying methods on the specific energy consumption (MJ/kg$_{water}$) are given in Fig. 3. As it can be seen there, the SEC for HAD, IRD, VD, FD, HAD2-FD, HAD3-FD, HAD4-FD, IRD5-FD, IRD10-FD, IRD15-FD, VD2-FD, VD3-FD and VD4-FD was 73, 40.7, 167, 496.1, 381.7, 324.5, 289.7, 295.9, 253.4, 233.6, 425.2, 355.8, and 331.5 MJ/kg$_{water}$, respectively. It can be seen that as the drying time decreases, the total specific energy consumption decreases. In the case of combined drying, the energy consumption of the given method decreases significantly ($p<0.05$) with the increase of the pre-drying time (from 2 to 4 hours and from 5 to 15 min). The highest SEC was recorded in the FD compared to other drying methods (SEC=496.1 MJ/kg$_{water}$). So it is very important that improve freeze-drying – very energy intensive process – by reducing energy consumption and drying time.

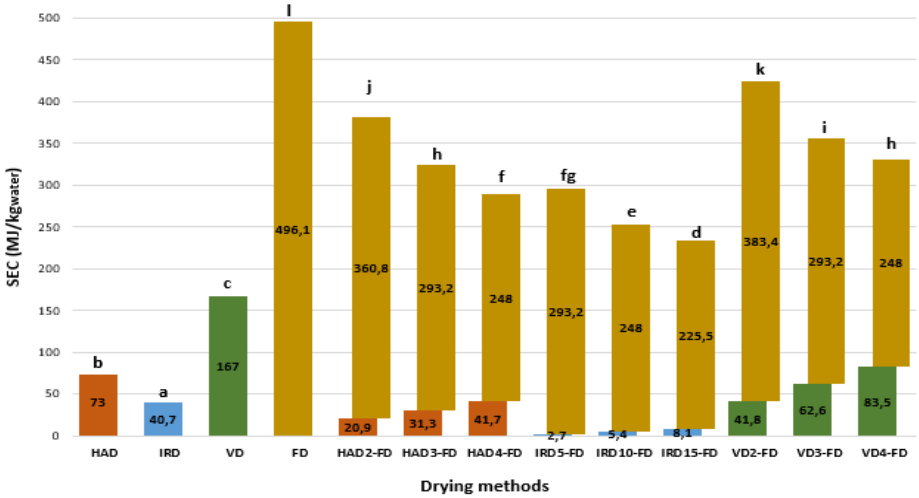

Figure 3. Effects of different drying techniques on the specific energy consumption (SEC) of dried blueberries
Bars with different letters differ significantly from each other as determined by Duncan's test.

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The reason for the high energy consumption of lyophilization is that, it usually uses electric heating plates to provide the heat required for ice sublimation, with low heat conductivity [18]. In freeze-drying, the basic energy, which required to remove 1 kg of water is almost double that of conventional drying (e.g. HAD) [19]. In this study, the specific energy consumption of the FD is about 6.8 times the energy consumption of the HAD. The lowest SEC was related to the IRD-FD technique. The energy consumption of the IRD15-FD is 52.9 % lower than the energy consumption of the FD, there is a significant difference between them.

3.3. Rehydration ratio (RR)

Rehydration ratio (RR) is important quality evaluation index for dehydrated products. This means that the higher the RR, the better the quality of the dried material. The Fig. 4. showed the RR of blueberry samples under different drying methods. The rehydration ratio values obtained in this work varied from 1.43 to 3.67. The maximum rehydration rate (3.67) was obtained for VD2-FD, the RR value of FD was 3.54, but there was no significant difference ($p>0.05$) between them. The rehydration rate of the vacuum pre- and freeze-dried product is particularly high, differing significantly ($p<0.05$) from the RR of the other combined dried samples. It was observed that rehydration ratio of IRD-FD and VD-FD decreased with increasing of drying time at pre-drying, with the exception of HAD-FD.

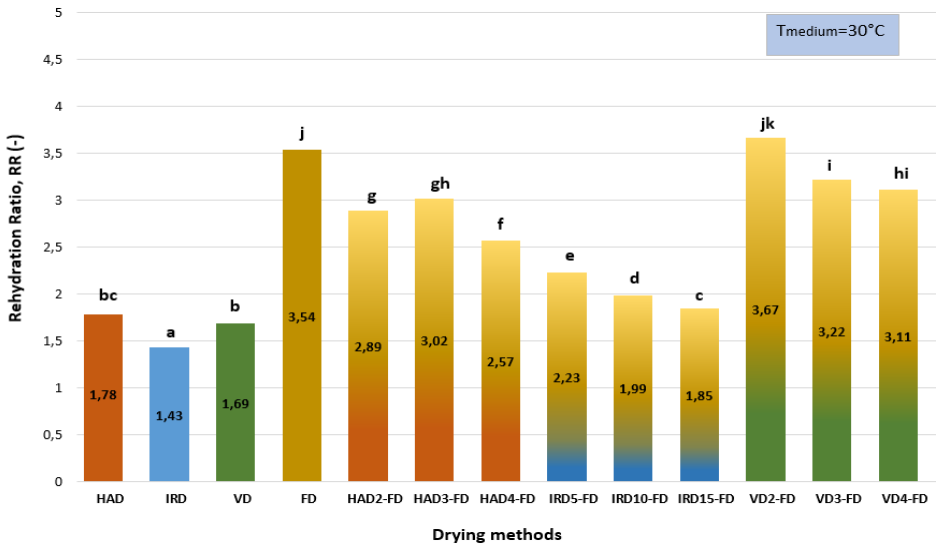

Figure 4. Effects on different drying methods on the rehydration ratio of dried blueberry samples
Bars with different letters differ significantly from each other as determined by Duncan's test.

Dried blueberries with single-stage IRD, characterized by the lowest rehydration rate (1.43) compared to other single-stage (HAD: 1.78, VD: 1.69) methods used in the present study. After 3 h of soaking in water, the rehydration capacity of blueberries dried by single-stage HAD at 60°C and 1 m/s was 2.30 [20]. The relatively low rehydration ability of single-stage infrared-, vacuum-, and hot-air dried blueberries is primarily due to collapse structures and shrinkage [21, 22]. Based on the results, it is not surprising that the rehydration index of freeze dried blueberries is high. Similar finding has been reported by Rajkumar et al. [23] on carrot drying. This can be caused by porous structure, and surface micro capillaries as a result of the freeze dried (FD) method [24]. As a result, the freeze dried material can be quickly restored to its original, raw state. In addition to FD products, the same can be said for VD-FD materials.

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4. CONCLUSIONS

In this study, whole blueberries were dehydrated by single-stage hot air-, vacuum-, infrared-, and freeze-drying, and these drying methods were also combined. Compared with freeze drying (FD), the infrared-freeze drying (IRD-FD) could effectively lower the drying time and total energy consumption, especially IRD15-FD. The IRD15-FD reduced the drying time by 53.4%, besides consuming less energy (52.9%) compared to single-stage freeze drying. It was found that the drying time of the HAD-FD material was similar to that of the VD-FD samples. The specific energy consumption (SEC) of HAD4-FD was the same as IRD5-FD. Vacuum pre- and freeze-dried (VD2-FD) blueberries have a water absorption capacity better than FD, IRD-FD and HAD-FD were dried. Although the rehydration of lyophilized blueberries (RR=3.54) is almost the same as that of vacuum pre- and freeze-dried blueberries (RR=3.67), its energy consumption is 1.17 times. The rehydration rate (RR) of the HAD-FD samples were close to the VD-FD samples. Taking into account the economic and quality factors, the VD4-FD, HAD3-FD and IRD5-FD a good option for use in the food industry. Further experiments are needed to optimize the combined drying.

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EMISSION CHARACTERISTICS OF SPARK-IGNITION ENGINE RUNNING ON PLASTIC WASTE PYROLYSIS OIL AND GASOLINE BLENDS

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ABSTRACT

The utilization of liquid products as transportation fuel derived from the thermal decomposition of different plastic waste mixtures was investigated. The production of pyrolysis oils was performed in a laboratory-scale batch reactor utilizing polystyrene (PS), polypropylene (PP), and high-density polyethylene (HDPE) waste blends. Two different mixtures (10% PS – 60% PP – 30% HDPE; 10% PS – 30% PP – 60% HDPE) were prepared, and the influence of reflux was also studied. The pyrolysis oils were blended to commercial gasoline in the 0-100% range. It was found that each blend could be successfully used as an alternative fuel in a traditional spark-ignition engine without any prior modifications or fuel additive. However, based on the engine tests, the presence of the reflux is vital as the composition of the pyrolysis oil is closer to the commercial gasoline. The emission measurements showed increasing NO_x emissions compared to neat gasoline, but, on the other side, a decrease in CO was noticed. These changes were much smaller in cases when reflux was used during oil production. Based on the obtained results, the utilization of reflux-cooling is an effective method to enhance the gasoline range hydrocarbons in the plastic waste pyrolysis oils, and therefore blending these oils to commercial gasoline might be viable.

Keywords: plastic waste, recycling, pyrolysis, emission

1. INTRODUCTION

According to the research of „Our World in Data” [1]: while plastic production was 2 Mt in the 1950’s, this amount reached 381 Mt in 2015. Additionally, between 1950 and 2015, the world produced 7.8 billion tons of plastics, which is more than one ton for every person today. Based on the current statistics [2], roughly 9% of plastic waste has been recycled since 1950. Although the degree of recycling and energetic utilization was undoubtedly increased in the last few years, new waste processing technologies arise, such as pyrolysis, which is a promising method to generate transportation fuels from plastic wastes.

The pyrolytic products can be divided into gas, liquid, and solid fraction. Based on the process parameters the gas/liquid ratio can be changed. It was shown in a previous study that the gasoline to diesel ratio in pyrolysis oils could be significantly affected by changing the reflux temperature [3]. Generally, lower reflux temperature generates more gasoline range hydrocarbons in pyrolysis oils, but the intensive molecule scission also produces more short-chain molecules appearing in the gas phase. The literature reveals that the pyrolysis oils blended with conventional fuel could be used for transportation and engine tests even with neat pyrolysis oils are reported. Budsaereechai et al. [4] tested neat pyrolysis oils from HDPE, LDPE, PP, and PS in diesel and gasoline engines. It was shown that the gasoline engine worked only with the PS oil, while the HDPE, LDPE, and PP oils worked only with the diesel engine. A multi-cylinder spark ignition engine was utilized by Kumar et al. [5] to investigate the oil-gasoline blends. The engine operated without any modifications with 0-20% pyrolysis oil in gasoline, and it was noticed that NO_x emission increased and hydrocarbon emission decreased as the concentration of pyrolytic oil in gasoline increased. Kaimal et al. [6] investigated the influence of pyrolysis oil addition to the diesel fuel by

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utilizing a compression-ignition engine. The pyrolysis oil content ranged from 0 to 100%. It was found that although the engine was able to run on neat pyrolysis oil, the 25% oil blended with diesel showed better results than other blends compared to commercial diesel fuel.

The utilization of pure pyrolysis oils is highly desired due to no additional oil separation steps are involved in the fuel production process, such as distillation. In fact, the distillation of pyrolysis oils enhances the quality of the product, which might be even closer to standard regulations, but the utilization of neat pyrolysis oils is also in the focus of recent researches. This study investigates the performance and emission properties of a spark-ignition engine utilizing pyrolysis oils blended with commercial gasoline in 0-100% portion.

2. MATERIALS AND METHODS

The pyrolysis runs were performed in a laboratory-scale batch reactor equipped with reflux. The vapors exiting the reflux are condensed in a water-cooled heat exchanger, and the liquid product (pyrolysis oil) is collected in a product container at room temperature. The remaining gases were collected in a sample bag and flared after the measurements. Fig. 1 shows the schematic illustration of the measurement system. The temperature of the reflux was adjusted to 150 °C in two cases to enhance the gasoline range hydrocarbons in pyrolysis oils. These runs were repeated without reflux cooling as well.

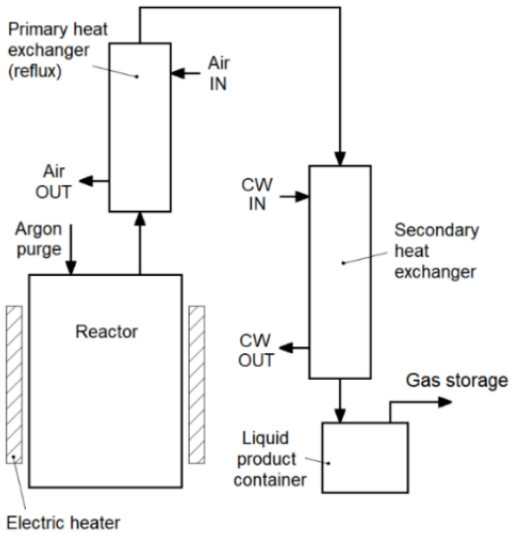

Figure 1. Schematic illustration of pyrolysis system used in this research.

Two plastic waste mixtures were used; one contained 10% PS – 60% PP – 30% HDPE, and the other contained 10% PS – 30% PP – 60% HDPE. These plastic types were separately gathered from local waste streams, and only the plastics with clearly visible identification codes were utilized. 200 g solid waste blend was loaded into the reactor in each case, then the reactor was flushed with nitrogen before measurement to eliminate the air from the system. The heat-up procedure started after the nitrogen flush, and the pyrolysis runs were typically stopped when the temperature inside the reactor reached ≈520 °C as the cracking reactions ended by this temperature.

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The pyrolysis oil and gasoline blends were tested in a traditional spark-ignition engine (Honda, GC-135) equipped with a carburetor. An electric generator was connected to the engine, while 500 W standard lamp was used as a load. Fuel consumption and exhaust gas emission (NO_x, CO, H_2, CH) during the engine tests utilizing oil/gasoline blends were measured and compared to the results obtained with commercial gasoline (RON=95). The NO_x emissions were monitored by Horiba PG-250 type flue gas analyzer, while the CO and H_2 were measured by gas chromatography (Dani Master) where a sampling bag was used to gather and store the flue gas. Additionally, the amount of CH content was measured by a hydrocarbon analyzer (model: Bernath Atomic 3002). The NO_x and CH emission measurement was based on MSZ EN ISO 8178-1:1999 standard method.

3. RESULTS AND DISCUSSION

The mass distribution of different products after the pyrolysis runs are summarized in Table 1. Based on the obtained results, it can be stated that the temperature of the reflux has a significant impact on the liquid and gas yield. The influence is not evident in the case of solid residues. Typically, the temperature of the pyrolysis vapors entering the water-cooled heat exchanger was 150 °C when the reflux was utilized, while the temperature reached 300 °C without reflux. The main goal of the reflux is to capture heavy hydrocarbon molecules and return them into the reactor for further molecule scissoring, which in situ increases the amount of C1-C4 products. Therefore the influence of the reflux can be investigated and compared to the thermal cracking without reflux cooling. Additionally, it can be concluded that the gas heating values are significantly higher when high portion of PP is present in the initial solid waste as PP typically generates C_3H_6 molecules.

Table 1. Pyrolysis summary of mixtures used in this study. The numbers in notation of concentration indicate the mass distribution of plastic types in each blends.

Mixture names	Product, W/W%			Reflux temperature, °C	HHV_{gas} MJ/Nm^3
	Gas	Liquid (oil)	Solid		
30PE-60PP-10PS	17.45	79.10	3.45	300	62.5
60PE-30PP-10PS	15.2	80.60	4.2	300	49.7
30PE-60PP-10PS-R	34.78	61.13	4.1	150	61.1
60PE-30PP-10PS-R	38.48	58.08	3.45	150	51.3

3.1. Engine test

Engine tests were performed to investigate the fuel consumption and emissions and compare them to commercial gasoline with RON=95. The volumetric fuel consumption change in the case of different oil/gasoline blends is shown in Fig. 2. It can be seen that fuel consumption is reduced by the growing amount of pyrolysis oil, compared to the consumption of neat gasoline. The fuel consumption was reduced by ≈10% in the case of neat 10PS-30PP-60HDPE.

Fig. 3 shows the influence of pyrolysis oil concentration at NO_x and CO emission measurements. Compared to the emission values of gasoline, pyrolysis oil concentration increase lead to higher NO_x emission. The most significant difference (by three times) in NO_x emission can be observed at the 100%

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pyrolysis oil in the case of 10PS-30PP-60HDPE. It can be stated that a higher amount of NO_x is shown at those blends containing more PE; moreover, this also referred to more intensive and higher temperature combustion. Additionally, the utilization of pyrolysis oils produced without reflux generated more soot, which can be elucidated with the presence of long carbon chains. The CO emission level decreased undoubtedly when pyrolysis oils produced without reflux were utilized. The CO is a toxic intermediary product that must be controlled according to health and environmental rules.

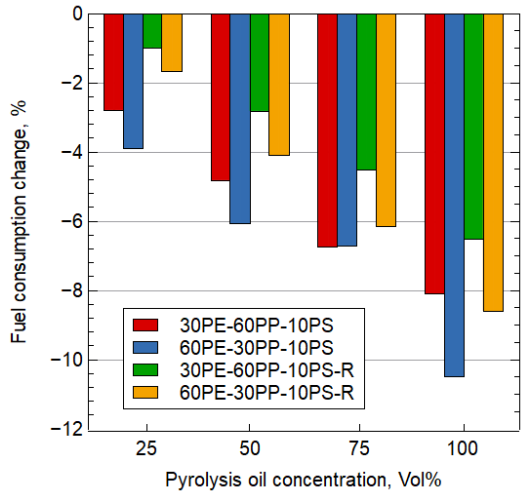

Figure 2. Effect of the pyrolysis oil concentration on fuel consumption trends. Typical fuel consumption of the engine utilizing traditional gasoline (RON=95) was 0,63 l/h.

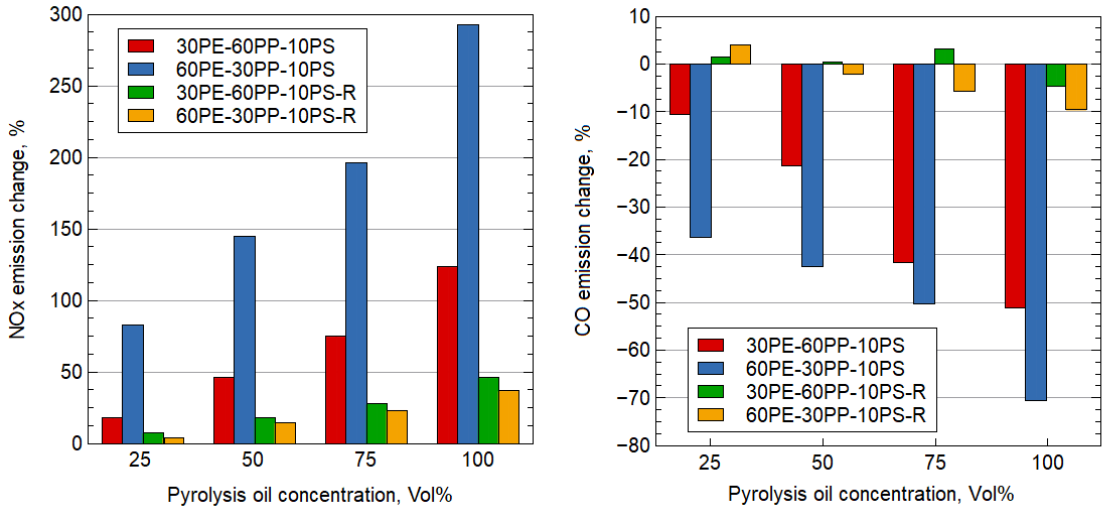

Figure 3. Left: NO_x emission change of the engine using various plastic gasoline compared to reference measurements. The typical NO_x emission of reference measurement was 124 ppm. Right: CO emission change of the engine using various plastic gasoline compared to reference measurements. The typical CO emission of reference measurement was 4,1 Vol%.

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Similar behavior can be seen in H_2 emissions (Fig. 4) compared to CO. The emitted H_2 is decreased by more than 70% in the case of neat pyrolysis oil produced without reflux. The measurement of CH emission (Fig. 4) presented unexpected results as an increase in trends was observed in almost all cases, except 60PE-30PP-10PS, where 25-50% oil blended to gasoline resulted in lower CH emission.

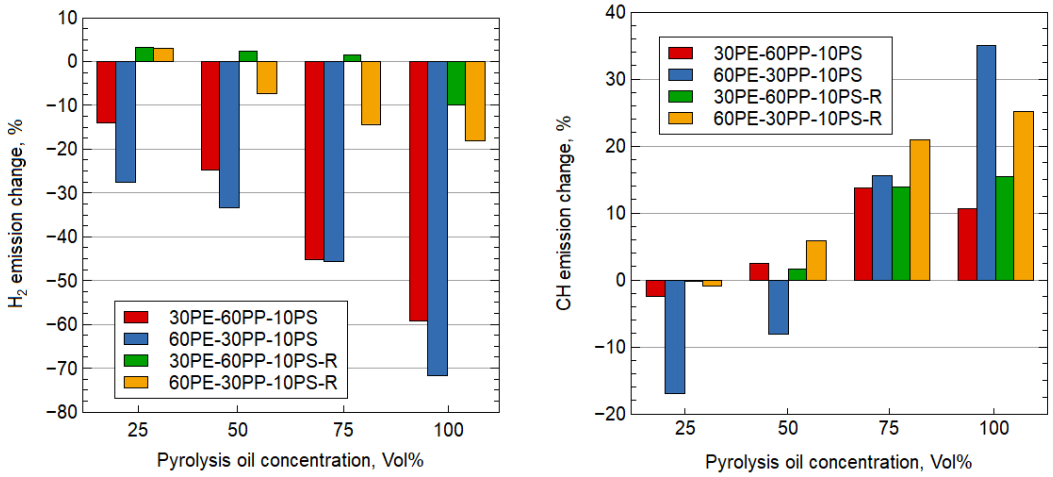

Figure 4. Left: H_2 emission change of the engine using various plastic gasoline compared to reference measurements. Typical H_2 emission of reference measurement with reflux was 1,2 Vol%. Right: CH emission change of the engine using various plastic gasoline compared to reference measurements. Typical CH emission of reference measurement with reflux was 763 ppm.

Based on the obtained emission measurement results, it was concluded that by utilizing the reflux during pyrolysis oil production the fuel blends show similar results compared to commercial gasoline. Although the engine was able to run in each case, the oils produced without reflux cooling showed significant differences. Thus, these oils should be blended to gasoline in a limited proportion.

4. CONCLUSIONS

In this study, two blends were made from the most common plastics, such as polystyrene (PS), polypropylene (PP), and high-density polyethylene (HDPE). The prepared blends were pyrolyzed in a batch reactor under different reflux conditions, and the produced pyrolysis oils were tested in a traditional spark-ignition engine using different oil/gasoline blends. It was concluded that the utilization of reflux significantly enhances the gasoline-range hydrocarbons in oils, and therefore the oil/gasoline blends provide closer emission trends compared with the no-reflux cases. Additionally, the fuel consumption decreased in all cases investigated in this study. It is worth noting that the obtained pyrolysis oils do not meet the criteria of standard transportation fuels, thus, upgrading the oils to improve the quality is recommended. The reflux geometry and operation might play an important role when high-quality pyrolysis oils suitable for transportation are desired.

ACKNOWLEDGEMENT

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EFFECT OF VIBRATION ON THE EFFICIENCY OF ULTRAFILTRATION

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ABSTRACT

Nowadays, several environmental challenges are present to cope with. One with outstanding importance is the protection of our water supplies, therefore examination of wastewater treatment technology is a priority, especially in the European Union. In this work, the effect of membrane module vibration amplitude on the efficiency of ultrafiltration (*UF*) was investigated in a vibratory shear enhanced membrane filtration system. Based on the results of model dairy effluent *UF* and statistical analysis, the maximum vibration level available resulted in the most efficient filtration process, due to the most significant reduction of membrane fouling. From our results it was observed that the permeate fluxes more than doubled, specific energy demand was roughly halved, with almost identical retentions for organic matter, and total filtration resistance was reduced to less than half. Results also showed that setting the optimal operating parameters, an advantageous, efficiency focused, and sustainable wastewater treatment technology can be established.

Keywords: vibratory shear enhanced processing, ultrafiltration, dairy wastewater treatment, operational parameter analysis

1. INTRODUCTION

For the protection of our ecosystem, the protection of drinking and living waters has a special role. Food industry uses huge amount of water to meet high hygiene regulations and due to individual technological needs. According to United Nations Environment Programme (*UNEP*) [1], dairy industry is no exception, and its wastewater, if released into nature, poses a high environmental risk (e.g., eutrophication), due to its high organic content, but it is also a potential starting point for a circular economy by reusing valuable constituents. The use of membrane separation processes can be an excellent solution for the treatment of dairy wastewater [2, 3], as it reduces the load of organic matter, can be integrated into existing, continuous technology, and requires little or no addition of chemical compounds. The membrane itself is a semipermeable partition wall that separates components depending on their molecular weight cut-off (*MWCO*), material and the filtration circumstances. The *UF* method is based on mainly size exclusion, but reversible and irreversible reactions happen between the membrane surface and particles of the wastewater. In addition to its many advantages, the most significant disadvantage is membrane clogging/fouling, which greatly limits its long-term, large-scale applicability. There are basically three approaches to reduce blockage: optimizing the membrane material in order to minimize the attraction interactions, pretreating the wastewater to remove the most active clogging reagents and improving the design and operation of the membrane module, which reduces clogging through more efficient hydrodynamic flow [4]. Applied vibration is an example for improved module design and operation which was found beneficial by [5] and [6] in comparison with traditional procedures. Results from [7] shows that using a vibratory shear enhanced processing (*VSEP*) system decreased concentration polarization, the filtrate flux increased along with the transmembrane pressure and compared to conventional cross-flow filtrations, the energy consumption of *VSEP* was found to be significantly lower. As reported by [8], analysis with scanning electron microscope of the morphology of the membrane surface showed that without vibration, particles

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were placed in a tight, dense manner while vibration was applied a more open, scattered particle distribution was observed. As stated by [9], despite having many advantageous properties, the *VSEP* technology is the sole property of an American company (New Logic Research, Inc.) and for this reason, research is relatively limited, but with the accumulation of appropriate theoretical and practical knowledge, a new, widely available technology could be developed. In our laboratory research, we aimed to investigate the effects of induced shear rate on the membrane surface, which can be resulted by membrane module vibration, while the main driving force of the process is the transmembrane pressure (*TMP*). The effect of vibration was investigated for efficiency parameters such as filtrate fluxes, membrane rejections for organic matter and milk constituents, values of specific energy consumption, and membrane filtration resistances. Our goal was to study and interpret the data obtained during laboratory work in order to find out which set of operating parameters, vibration amplitude and *TMP*, results in the most efficient filtration process due to the reduction of membrane fouling.

2. MATERIALS AND METHODS

2.1. Vibratory shear-enhanced processing (*VSEP*) membrane separation

Membrane separation tests were carried out on *VSEP* laboratory mode device (New Logic Research Inc., *USA*) with 30 kDa *MWCO* polyether sulfone membranes. Filtrations were performed in each case starting from 10 litres of freshly prepared and homogenized model wastewater made of concentration of 5 g dm^{-3} skimmed milk powder and 0.5 g dm^{-3} anionic detergent. The experiment setup, based on earlier studies, consisted of the combination of three vibration and the four *TMP* levels, resulting 12 separate experiments. Detailed parameters of the experiment series are in Tab. 1. Two-way analysis of variance was used to evaluate the measurements and calculated data of the mean values of each level with a confidence interval of 95% confidence level with Statistica 13.4 software (*TIBCO* Software Inc., *USA*).

Table 1. VSEP experiment setup with operating parameters

Parameter	Value											
$A_{vibr.}$ [m]	0.0000				0.0127				0.0254			
TMP [MPa]	0.6	0.8	1.0	1.2	0.6	0.8	1.0	1.2	0.6	0.8	1.0	1.2

2.2. Efficiency parameters

a) Permeate fluxes: An important parameter in wastewater treatment is the amount of filtrate, which calculated for unit of time and membrane surface area is called flux, as in Equation (1). This characterizes the permeability of the membrane under certain conditions. A general goal is to produce as much filtrate as possible, but of course, total efficiency depends on energy investment and the permeate quality also.

$$J_{perm} = \frac{TMP}{\eta \cdot (R_M + R_{IRR} + R_{REV})} \quad (1)$$

, where J_{perm} is the permeate flux [$m^3m^{-2}s^{-1}$], *TMP* is the transmembrane pressure [Pa], η is the dynamic viscosity of the solvent at 25 ° C [Pas], R_M is the membrane intrinsic resistance [m^{-1}], R_{IRR} is the irreversible resistance, which cannot be removed by rinsing, only by chemical treatment [m^{-1}] and R_{REV} is the reversible clogging resistance [m^{-1}], which is formed from the surface of the membrane due

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to the removable polarization layer. Reversible and irreversible resistance values vary depending on flow conditions, pressure difference, temperature, and solution properties.

b) Specific energy demand: it is economically and environmentally important to know how much energy is needed for production. In the case of membrane filtrations, this can be specified per unit of treated wastewater, the amount of filtrate. In our work, the specific energy consumption is used to generate 1 m^3 of filtrate calculated by Equation (2). Our goal is to achieve the lowest possible energy consumption. It is a question whether the flux increment is sufficient as a result of the vibration-reduced clogging or the use of extra energy by the vibromotor increases costs too much.

$$e = (P_{FP} \cdot \eta_1 + P_{VM} \cdot \eta_2)/(A \cdot J) \quad (2)$$

, where e is the specific energy consumption [kWh m^{-3}], P_{FP} is the actual power of the feed pump [kW], η_1 is the pump efficiency [%], P_{VM} is the actual power of the vibromotor [kW], η_2 is the efficiency of the vibromotor [%], A is the membrane filtration surface [m^2], J is the permeate flux [l m^{-2} h^{-1}].

c) Membrane rejections: The tendencies of rejections, also known as retentions, which determine the quality of the filtrates, give an insight into the selectivity of the membrane under given condition. They show the percentage of a given component remaining in the concentrate relative to the starting solution by Equation (3). Our goal is to achieve the highest possible retention values, thus producing the clearest possible filtrate. Obviously, in line with what has been said so far, the filtration process must also be productive both in an economical and a sustainable way. In our experiments two types of rejections were calculated, one, rejections of organic matter based on chemical oxygen demand (*COD*), in order to control harmful environmental emissions, and two, the rejection of dairy particles in order to extract potentially recoverable parts that would otherwise go to waste. Rejections only for organic content will be later discussed.

$$R = \left(1 - \frac{c_P}{c_F}\right) \cdot 100 \quad (3)$$

, where R is the rejection [%], c_F is the concentration of the feed solution, c_P is the concentration of the permeate and the concentrations are always in the same dimension (e.g., [mg l^{-1}]).

d) Filtration resistances: In order to explore the sustainability of the filtration process and the possibility of long-term, industrial operation, we also calculated filtration resistances. Based on the resistance model, the flux of the permeate is, among other effects, inversely proportional to the value of the total resistance. The degree of total resistance depends on the type and degree of membrane clogging. There are three parts to total resistance indicated in Equation (4): the membrane's own resistance (which is constant under given conditions as in Equation (5)), reversible, and irreversible resistance. The reversible resistance is due to the concentration polarization layer formed on the surface of the membrane, it can be washed off and removed from the surface of the membrane calculated by Equation (6). Irreversible resistance is created by parts that clog the inner pores of the membrane, and its name characterizes the final, difficult-to-remove property of the clog, calculated by Equation (7). General goal is to minimize total resistance, and within that, to reduce the rate of irreversible resistance. Resistance values were calculated from data of water fluxes with the membranes before and after the ultrafiltration experiments with Equations (4-7).

$$R_T = R_M + R_{IRR} + R_{REV} \quad (4)$$

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$$R_M = \frac{TMP}{J_{before} \cdot \eta_W} \quad (5)$$

$$R_{IRR} = \frac{TMP}{J_{after} \cdot \eta_W} - R_M \quad (6)$$

$$R_{REV} = \frac{TMP}{J_{constant} \cdot \eta_{WW}} - R_M - R_{IRR} \quad (7)$$

, where R_T is the total, R_M is the membrane, R_{IRR} is the irreversible and R_{REV} is the reversible resistance [m^{-1}]. J_{before} is the measured water flux before, J_{after} is the measured water flux after filtration and $J_{constant}$ is the stabilized permeate flux during filtration [$m^3m^{-2}s^{-1}$], η_W is the dynamic viscosity of water, η_{WW} is the dynamic viscosity of model dairy wastewater at 25 °C [Pas].

3. RESULTS AND DISCUSSION

3.1. Permeate fluxes

On Fig.1 flux values are shown. On average, without vibration fluxes were 22.4 $lm^{-2}h^{-1}$, with intermediate vibration 40.7 $lm^{-2}h^{-1}$, and with maximum vibration 47.8 $lm^{-2}h^{-1}$. It is visible that the maximum vibration amplitude resulted in the highest mean flux value, which is more than two times than without vibration. Based on two-way analysis of variance, the effect of different vibration levels resulted in significant differences between the filtrate flux values ($p < 0.05$), the significant difference is between 0 m and 0.0127 m, and 0 m and 0.0254 m amplitude levels. We can deduce the effect of vibration on reducing membrane clogging. According to [10], during this process, the filtered liquid remains almost stationary compared to the intensely vibrating membrane, so the surface shear force is greatly increased, as a result of which the clogging particles are removed, the concentration polarization decreases and the amount of permeate increases.

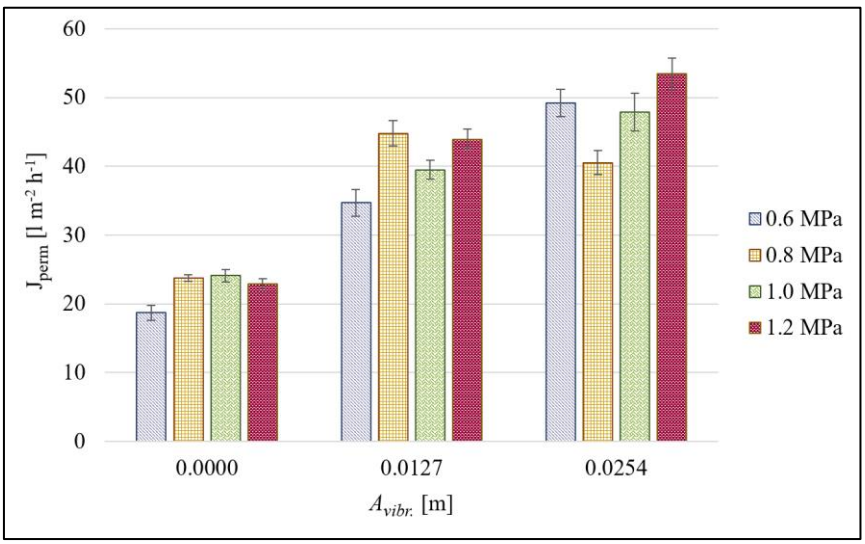

Figure 1. Permeate flux change as function of vibration amplitude (MWCO: 30 kDa; q_{Vrec}=0,9085 m^3h^{-1}; T=25±1 °C)

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3.2. Specific energy demand

Shown on Fig. 2. specific energy consumption values were on average 0.70 $kWhm^{-3}$ without vibration, 0.43 $kWhm^{-3}$ with intermediate vibration, 0.38 $kWhm^{-3}$ with maximum vibration. It is visible that the maximum vibration level resulted in the lowest energy consumption, which is almost half of the average value measured without vibration. Based on the two-way analysis of variance, the effect of different vibration levels resulted in a significant difference between the specific energy consumption values ($p < 0.05$), the significant difference is between 0 m and 0.0127 m, and 0 m and 0.0254 m amplitude levels. Interestingly, as specific energy demand is calculated per filtration volume, the additional amount of energy used by the intensified vibration could improve efficiency as it derived multiple increasement in permeate flux in proportion to the energy used by the vibromotor.

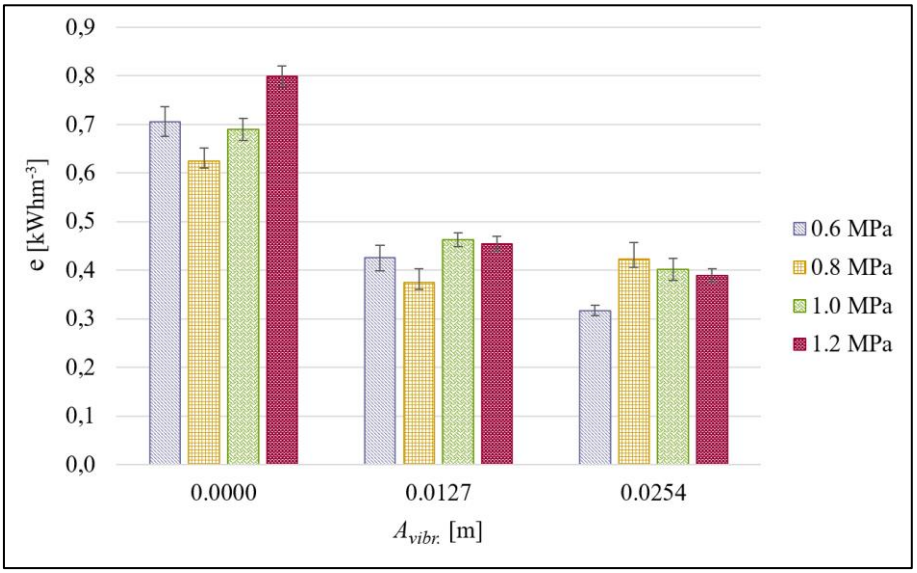

Figure 2. Specific energy demand change as function of vibration amplitude (MWCO: 30 kDa; qVrec=0,9085 m^3h^{-1}; T=25±1 °C)

3.3. Membrane rejections

Controlling adverse environmental effects is a priority in wastewater treatment, for organic matter emission rejections are calculated by chemical oxygen demand. Our results are shown on Fig. 3. The average rejection values for organic matter per vibration level were 70.8% without vibration, 73.1% with intermediate vibration, and 71.3% with maximum vibration. Based on the two-factor analysis of variance, the effect of different vibration levels did not result in a significant difference between the retention values for organic matter ($p > 0.05$). Due to differences in filtration types and other mechanisms yet to be explored, our results are very similar, apparently independent from the effects of vibration.

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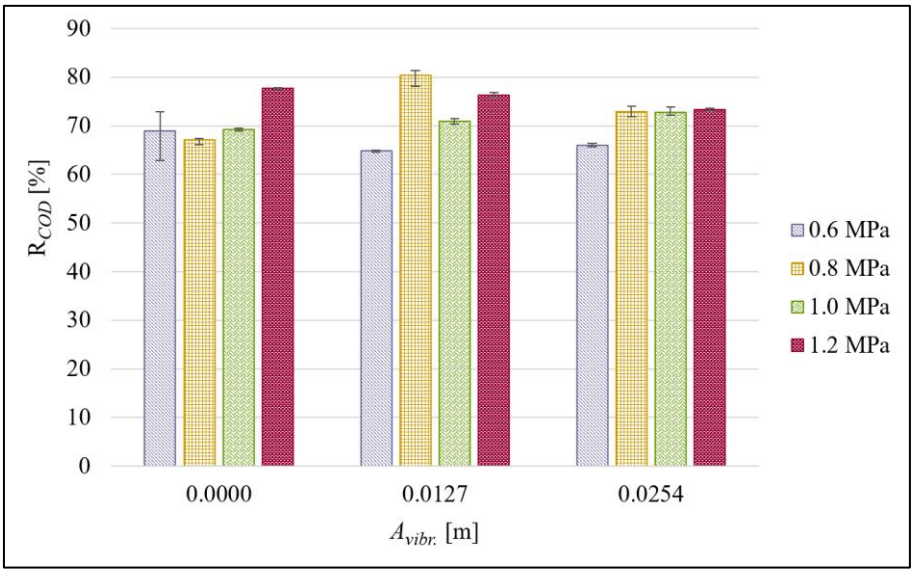

Figure 3. Membrane rejection for chemical oxygen demand change as function of vibration amplitude (MWCO: 30 kDa; qVrec=0,9085 m^3h^{-1}; T=25±1 °C)

3.4. Filtration resistances

On Fig. 4, the total filtration resistance values are illustrated according to the three vibration amplitude levels to provide a more insightful analysis of the effect of vibration. Total resistance consists of three parts. First, the membrane's own resistance, which is constant under given conditions. Second, the reversible resistance caused by concentration polarization formed on the membrane surface, which can be washed off and removed. Third, the irreversible resistance, which is created by parts that clog the inner pores of the membrane, and its name characterizes the final, difficult-to-remove property of the clog. The average total resistance values on vibration levels were $170 \cdot 10^{13}$ m^{-1} without vibration, $102.4 \cdot 10^{13}$ m^{-1} with intermediate vibration, and $76.4 \cdot 10^{13}$ m^{-1} with maximum vibration. The maximum vibration level resulted in the lowest total resistance, which is less than half without vibration. Within this, the ratio of reversible to irreversible resistance is important.

We observed a trend that with increasing vibration, the value of reversible, easily removable resistance decreased greatly, while the values of irreversible resistance decreased slightly in the same way. The trend is certainly due to the vibration-induced membrane clogging reduction and the change in membrane surface flow conditions. Based on the two-factor analysis of variance, the effect of different vibration levels resulted in a significant difference between the values of reversible and irreversible resistance in addition to the total filter resistance ($p < 0.05$). For all three resistance values, the significant difference is between 0 m and 0.0127 m, and 0 m and 0.0254 m amplitude levels.

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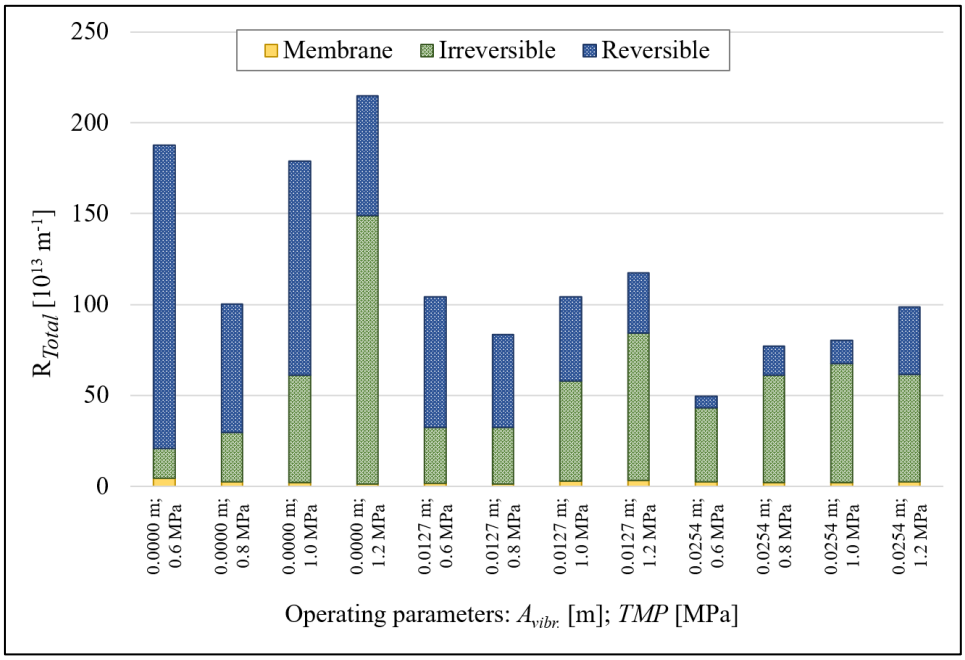

Figure 4. Membrane resistance change as function of operating parameters (MWCO: 30 kDa; qVrec=0,9085 m^3h^{-1}; T=25±1 °C)

4. CONCLUSIONS

The effect of the vibration amplitude for filtration efficiency was investigated by *VSEP* ultrafiltration with model dairy wastewater. 12 separate experiments were executed, and results were analysed statistically to establish trends to characterize best available operating parameters that ensure adequate performance. Four efficiency parameters were studied. First, the permeate flux, which also characterizes the amount of treated wastewater and the time course of filtration. The second indicator is of economic and environmental significance, this is the specific energy consumption, which can be used to compare different treatments per unit of treated wastewater. The third indicator is the membrane rejection, which characterizes membrane selectivity, also for organic materials to control harmful environmental emissions, as well as for milk producers, due to the recovery of potentially recoverable valuable components. Lastly, the type and severity of total, reversible, and irreversible filtration resistances, which can provide a picture for a long-term, industrial operation. Based on our results, the maximum vibration level resulted in the most efficient filtration process for all four parameters. As a result of reduced membrane clogging due to vibration, permeate fluxes more than doubled compared to the least efficient process, specific energy consumption was roughly halved, with almost the same, standard rejection values, and total filtration resistance was reduced to less than half. The beneficial effect of applied vibration in ultrafiltration is remarkable and further investigation of other operating parameters can help establish an economical wastewater treatment technology that will also serve sustainable development and the protection of our environment in the long run.

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THE ERASMUS PROGRAM AND ITS EFFECT TO THE LABOUR MARKET

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ABSTRACT

In our work, we deal with the question of what impact the Erasmus programme has on linguistic and personal competences and how it helps the economy forward. We look around this topic in the literature review. We managed to get almost 100 surveys filled out among the participants however, the representatives of the companies proved to be quite passive, with only nearly 30 of them replying. In the form of a survey, we found that it has a positive effect on improving language skills and helping with independence or problem-solving ability. In the quantitative survey we found that companies often prefer other factors than the people in a mobility programme, and they do not show favour toward a mobility student in a job interview, although the skills acquired during the programme help the person. Therefore though indirectly, but the programme has a positive impact on the economy as well.

Keywords: Erasmus program, students, labour market, quantitative survey

1. INTRODUCTION

Open worldview. What is this and how can we get it? Open worldview helps taking the thread of conversation forward. Healthy debates can be conducted by substantiating our thoughts with arguments, and meanwhile, we try to understand the other's aspect as well. We can meet a lot of people in our university years, who have already experienced a lot, and they are ready to give their knowledge to the new generations. If we listen to their thoughts with an open soul, we can gain much more than learning a profession. We can prepare for measurable moments in our lives, even if it is a job interview, a job loss or family issues. We believe, the ERASMUS program means a similar openness - to the world.
In our study, we try to answer the following questions:

- When and how was the Erasmus program established?
- What numerical data characterizes the Erasmus program?
- How participants see the impact of the program?
- What are the competencies and factors that employers prefer in a job interview?

1. 1. The creation and background of the Erasmus

The name of Erasmus is a term with multiple meanings. On the one hand, a tribute to the traveling scientist, theologian and philosopher Desiderius Erasmus (1466-1536) [1]. However, ERASMUS can also be interpreted as an abbreviation of the European Community Action Scheme for Mobility of University Students, which means that the European community action plan for the mobility of university students [2]. According to Jacques Delors, who is a French politician, and the 8th President of the European Commission, students mobility has been a priority since 1985. In his experience, the issue of European integration was best understood by university students, and he believed that if they are given space and opportunity for the mobility, it could create a true European spirit [3]. During his work (1985-1995), the draft of Erasmus program was developed as part of the "People's Europe" concept. One of the aims of People's Europe was to bring European integration closer to the citizens thus, the Erasmus program fits

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perfectly with the ideas and the economic policy interest as well, which would increase students mobility and the flow of skilled workforce.
This would also stimulate integration and economic processes. The draft of Erasmus program was prepared under the supervision of Irish Commissioner, Peter Sutherland and perhaps it is thanks to him that the program has been so successful [1].
At that time, the European Economic Community was still a purely economic association, not a political one, so there was little willingness in them to include the education in their jurisdiction as well. Sutherland decided to launch the initiative at a conference of the European Students Association in Paris, and hundreds of students enthusiastically welcomed it. In 2016, he told to the University College Dublin's newspaper that although it proved difficult, one of the greatest successes of his life was launching the Erasmus program. He knew that the final goal was not just the education, but to expand European integration and developing a new attitude in the EU, which we are still shaping today. Sutherland, who also referred as the "father of Erasmus", sees a need to young people recognize and see a common cultural and value-based system, which shared by the European countries and they do not feel foreign or different from others. Everyone has a sense of nationality. The real aim of European integration is to tame nationalism and make it easier to understand different cultures in a non-hostile way [4]. The implementers of the Erasmus+ program are: European Commission, the national agencies, Euridyce network, Youth Wiki National Correspondents Network, eTwinning Support Services, The School Education Gateway (SEG) and the EPALE /Electronic Platform for Adult Learning in Europe/ [5].

1.2. Erasmus in numbers

Initially, 11 European countries (Belgium, Denmark, the United Kingdom, France, Greece, the Netherlands, Ireland, Germany, Italy, Portugal and Spain) joined the program (EB factsheet, 2017). Today, 34 countries can participate in all Erasmus + activities and in addition, more than 100 other countries with certain criteria [6]. In the first year, 3,200 students participated in the program already, and in more than three decades, 9 million people can say that they have taken the advantage of the opportunities offered by the Erasmus program. The program gives open doors to high school students, students in higher education and vocational school students, volunteers, youth helpers, teachers and trainers. They can spend their time not only in educational institutions within the framework of the program, but also as an intern in companies, thus help them to find a later job in the labor market[7]. In 2017, the program celebrated its 30th anniversary, and because of it, the European Commission issued a brochure, this gives information about how successful the Erasmus has been. In three decades, 9 million people have already participated in the Erasmus program, which mean:

- 4.4 million students in higher education,
- 1.4 million exchange program,
- 1.3 million students in vocational training,
- 1.8 million teachers or youth helpers
- 100,000 volunteers and
- 100,000 Erasmus Mundus students and participants. (Fig. 1.)

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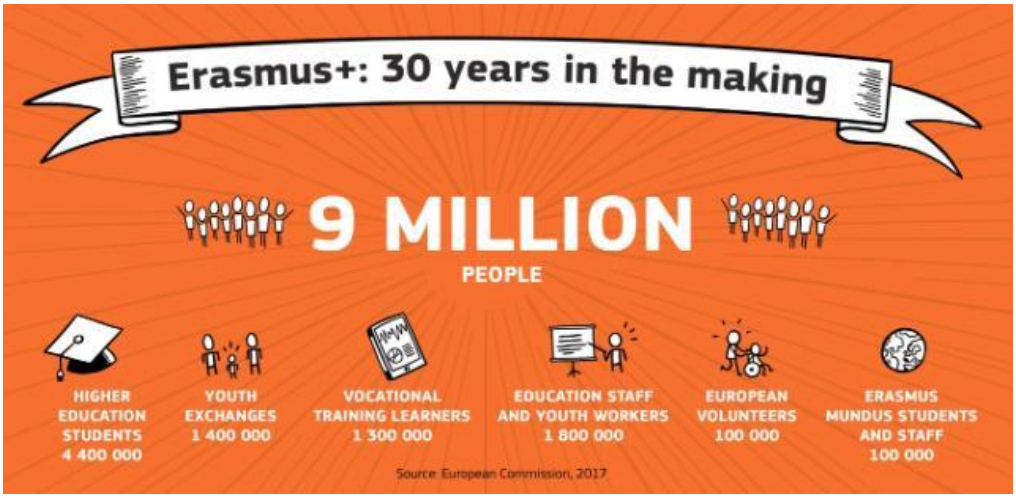

Figure 1. 30 years in Erasmus Source: [8]

1.3. The relationship between the Erasmus and getting a job

According to a 2017 European Commission briefing, participation in the program improve the career opportunities (Fig. 2). Students in the program are twice as likely to be placed in a year after graduation, than their peers who did not take the advantage of mobility. In addition, one-third of students who have completed an internship position within the program get a job opportunity from the company that employs them. According to their survey, Erasmus fellows earn 25% more and whether ¾ of the employers have found that including volunteer work in a CV (Curriculum Vitae) can be an advantage in gaining a position [9].

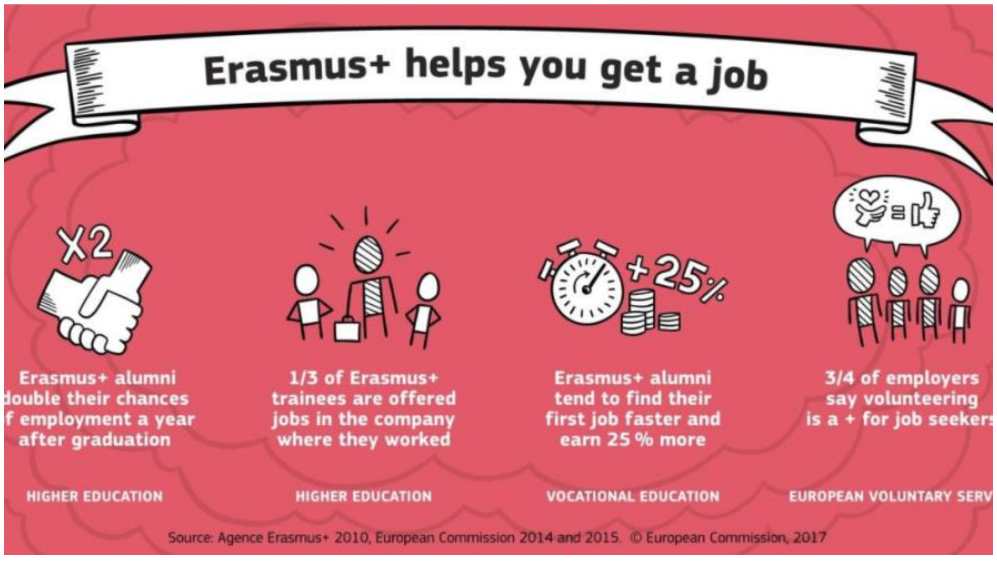

Figure 2. The Erasmus and the getting a job Source: [10]

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2. MEANS AND METHODS

When we complained the survey, we wanted to get a comprehensive picture of the opinions of the participants in the program and the employers too, so we decided to create two different surveys for the two different target groups. Moreover, we sought answers to questions such as what language and other competencies can develop during the Erasmus program and how these can be utilized in private life and in the workplace. What are the most important and most beneficial benefits of the program? I am interested in the perspective of both individuals and companies on these issues and the impact of the program on a country's economy. Does it have a stimulating effect or just hinder the country in its development?

2.1. The process and problems of data collection

When we chose the topic, we had already guessed that the number of responses would probably not be high, and unfortunately this was confirmed. The forms were created online, so the target groups were narrowed down to Internet users, but we cannot take this as a problem, because our future respondents are already be online. We found that the number of Erasmus participants in our circle of acquaintances is not high enough to collect 200 responses. Unfortunately, the possibilities of the Internet are also finite, and although we have shared the link in Erasmus-themed Facebook groups („Youth Bridges Budapest Erasmus+ ificsere,tréning & ESC önkéntes lehetőségek", „EnACT - Empowerment through Nature Authentic Communication and Theatre") and 42 of our own acquaintances also shared our request, we could receive only 89 responses. Our application to other groups may not have been accepted. We sent our request to Erasmus + Youth and Eurodesk also in the hope that they would have a platform where I could or they could have shared the link, but unfortunately nothing was received from them, just an automatic system message. We realized another problem, when we searched employers. If we take any business for example, people in leadership positions do not devote energy to such issues. We primarily asked people who could see into a company's HR (Human Resource) department. Of course, we also used the possibilities of the internet here too: we sent e-mails to 569 (!) addresses. For the sake of diversity, we searched for contacts on the Business Directory website (http://www.uzletiszaknevsor.hu/), because here we can find businesses divided into categories. We tried to select multiple addresses from each area and we sent messages as an encrypted copy to about 50 recipients at a time. Unfortunately, an extremely large number of addresses were already found at the time of sending that these no longer exist, or the message has been marked as spam by the system. In total, 28 responses were received.

3. RESULTS AND DISCUSSION

3.1. Evaluate the responses of program participants

4/5 of our respondents were women, the rest were men, typically between the ages of 21-25. Our most frequently chosen destinations are Spain, France, Germany, Finland, the Netherlands, and the United Kingdom. Compared to the European Commission's report, the three most popular destinations among the Hungarians are Germany, Spain and Italy [5]. 83% of our respondents participated in higher education in the program as a student, 10% as a high school student, 5% as a student in a vocational school and 2% as a volunteer or youth helper. Among the options that could be marked that they work as teachers or as an instructor, but no one indicated it. From the responses to the duration, we found out that 11% of them spent between 6 and 12 months in the program, 89% are less than 6 months. In the following, participants were asked to rate their language competencies on a 1 to 5 scale. according to the fact, that after the time which spent in the program, their skills got worse, did not change, or developed (Fig 3).

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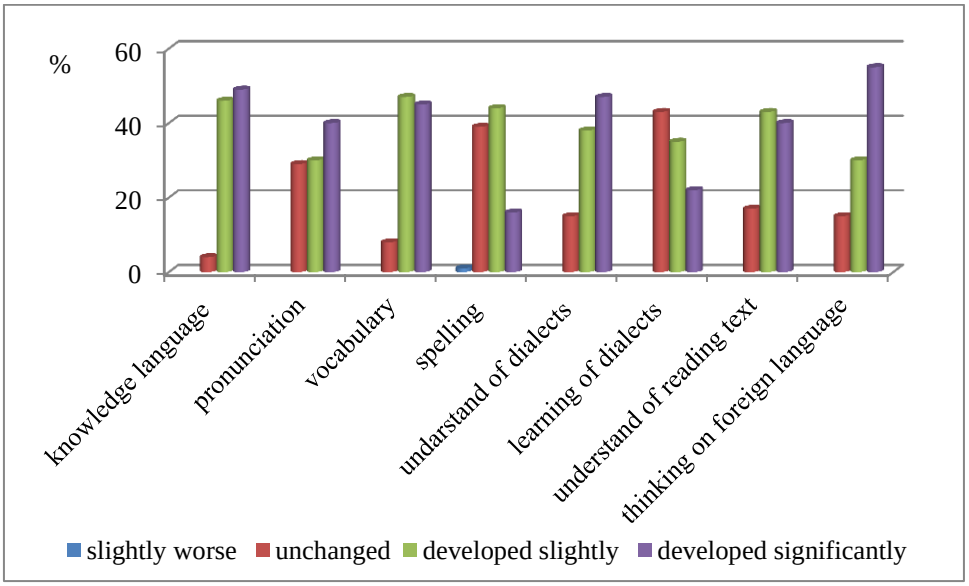

Figure 3. Distribution of respondents based on changes in each area of their language competence (%, N=89)

Taken together, only 19% of applicants showed no significant improvement in any skills, and there was only one person who felt that she or he had not developed in any area.

Not only the language but also other skills have greatly improved, according to the respondents. 70% of the participants said that the program is significantly improved their independence, because in a new environment they have to solve everything independently, for which they may have received assistance so far. Basically, it can be said that according to the opinion of research participants, the cultural awareness, communication skills, problem-solving skills, responsibility, teamwork skills and tolerance have also improved as a result of mobility. According to mobility practitioners, the most useful factors in the program are primarily getting to know another culture and improving language skills. The former was found useful by 93% of respondents and the latter by 91%. This is followed by the less professional benefits such as "Experience for Life", "Travel Opportunity", and "Making New Friends". Closely following the former benefits is that the applicant can get to know the education system of another country, which can also add a lot to her or his experience. The independence slipped to seventh place with 64%, but it is still high. Last but not least, with a relatively small percentage, which means 24%, 19% and 15%, the "Bridging the gate between countries", "Getting to know the economies of other countries" and "Getting to know the strategy and structure of other companies" close the line. These described terms are shown in Fig. 4.

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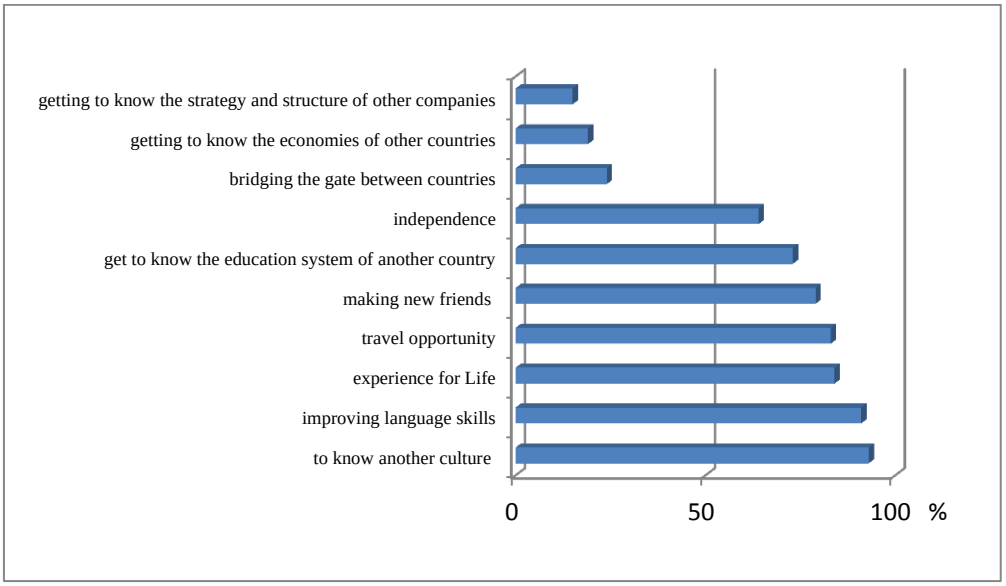

Figure 4. Distribution of respondents based on agreement with each factor and their importance (%, N=89)

The other part of the questionnaire was completed by those who are already working - 34 of those surveyed indicated this. They are typically located in highest proportion in marketing, education research, and finance area; however, health, beauty, agriculture and tourism are also represented at the fills.
The questions and the answers are presented together with the opinions of the employers, compared to them.

3.2. Description of employers' responses

Thus, a very small number of responses were received from employers. Almost half of the respondents were the owners and managers of the company, in addition, the heads of administration, heads of secretariat and HR managers answered our questions. About one-fifth of the enterprises operate in the capital city, 43% in county seat, 21% in city and the rest in smaller settlements. A significant proportion of them (68%) are small and medium-sized enterprises, while a quarter of them are medium-sized undertaking. In terms of scope of activities, we tried to gain broad insight into the opinions, we received returns from agri-food enterprises, IT companies, logistics service companies and from hospitality enterprises too. Regarding the specific issues, we obtained the following results.
About 25% of the respondents stated that they were indifferent to foreign relations. Accordingly, 32% stated that the prospective employee's language skills were a paramount importance, and 36% did not consider them. The possibility of participating in the Erasmus program is regularly raised by 7% as a question in job interview only. Only 1 company representative said that this fact was considered as a decisive factor when somebody wants to fill a position. In comparison, about 2/3 of the participants in the program indicated that they have talked about the Erasmus program participation and half of them feel that this factor mattered when they selected for the job. We asked the employers and employees too about the importance of the new and the emerging competencies developed during the Erasmus.

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For the company representatives, the language competence (75%), the development of independence (71%) and learning about the culture of another country (50%) are the three most important factors. In comparison, in the group of the program participants the problem-solving ability (74%), the development of communication skills (68%) and the aforementioned language competence and independence (62% - 62%) were in the top three. Interestingly, other values are considered useful by employers than participants. The difference is outstandingly high in the opinion of problem-solving ability, and about applicants could learn about the strategy and structure of other companies. For the latter factor, in front of the 43% corporate importance, only 15% of former students considered it as an important factor. On the one hand, this may be due to the fact that the employer has no benchmark for how the applicant may have had problem-solving skills before the program, they can only compare it with another employee. Furthermore, a person who has not done an internship abroad they cannot know the structure of other firms, they can only gain insight into the education system, so for them it is not as authoritative as for a leader.

4. CONCLUSIONS

According to the participants, the most important factors of the Erasmus program are that they can meet with other cultures, they can improve their language skills, gain a lifelong experience, they have an opportunity to travel and meet new friends, learn about another country's education system and become more independent. For 32-32% of companies the applicant's language is important or partially important, only 4% think it is decisive and 25% said that participation in the program can be a crucial factor in hiring a new employee. 50% of participants thought that the Erasmus program had contributed to get a position, and 56% said that the program was useful for finding a job. What is the reason of this difference of opinion? On the one hand, the already employed participants work in quite different areas than the responded companies, thus, such factor may be more important in the former areas than in other fields. Furthermore, in the first phase of the questionnaire we asked the mobility practitioners not only about language but also about the acquisition of other competencies, so it is possible if we consider these that they came to the conclusion that they developed several competencies, which although not directly, but contributed the acquisition of a position. In our opinion and based on a review of the literature, the Erasmus program has opportunities that we need to use in a long time run. Hungary has several indicators that indicate we are lagging the European average. Great educators in the education sector who are open to the innovation should be better valued because their goal is to develop with their students. Companies sometimes have too high expectations of interviewers, (for example 5 years of work experience), thus depriving the recent graduates from the opportunity instead of appreciating their energy invested in higher education and language learning. Unfortunately, new entrants in the labor market often lose motivation because their work is less valued because of the lack of professional experience. Yet young people who practicing mobility want to experience most of their tasks and works, because that is why they dared to spend several months in a completely foreign place with foreign language speaking. In our opinion, if companies knew more about Erasmus mobility, as an opportunity and a huge advantage, they would appreciate it better having such an experience.

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INFLUENCE OF ADDITIVES ON RHEOLOGICAL AND TEXTURAL PROPERTIES OF CELLULOSE BASED FAT MIMETIC

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ABSTRACT

Cellulose based fat mimetics play important role in substitution of fat in reduced fat food products. Production of food often includes application of additives. This work examines the influence of additives on the obtaining stable fat mimetic based on fibers of microcrystalline cellulose. Applied additives affect to the durability of food products and increase their shelf life. The influence of added additives was observed trough the rheological and textural properties of MCG fat mimetic, thus its further functional characteristics. Increasing concentration of fibers positively influenced to crosslinking during hydration and increased strength and consistency of obtained gel. But, application of small hydrophilic molecules of additives disturbed rheological and textural properties of fat mimetics. Obtained gels were still with the thixotropic behavior, but with significantly reduced viscoelastic properties, consistency, firmness and cohesiveness. Based on results, in the aim to ensure obtaining of stable, cross–linked gel of fat mimetic with adequate rheological, textural and functional properties, the mixture of additives is added after the hydration of fat mimetic gels, because of competition for polar water molecules between small additives molecules and available hydroxyl groups of cellulose chains.

Keywords: microcrystalline cellulose fat mimetic, additives, gel structure, rheology, texture

1. INTRODUCTION

Reducing the fat content and energy value of a food product implies the application of an adequate fat substitute. Ideal fat substitute should have all the functional characteristics of lipids, but also lower energy value, preferably 0 kcal/g. The functional properties that a fat substitute should have are sensory properties (odor and taste) and rheological properties (viscosity, consistency, texture). Also, fat substitutes should have emulsifying properties, to be thermostable, to allow dissolution of liposoluble aromas, vitamins, etc. [1, 2, 3]. The chemical structure of fat substitutes can be similar to lipids, proteins or carbohydrates and they are divided into two groups, group of fat substitutes and group of fat mimetics.

Fat substitutes are macromolecules that resemble to triglycerides (fats and oils) in both physical and chemical characteristics and that can theoretically replace fats in food on a one–to–one basis (gram–for–gram basis). They are obtained by chemical synthesis or enzymatic modification of fats and oils and labeled as "lipid–based fat substitutes".

Fat mimetics imitate the sensory and physical properties of fat, but they cannot replace the fat on a one–to–one basis. They are commonly labeled as "protein or carbohydrate–based" fat substitutes, where common food ingredients (starch or cellulose) have been previously chemically or physically modified to mimic the role of the fat. Their main characteristic is the great water absorption capacity. The energy value of the fat mimetics varies from 0 to 4 kcal/g [3].

Microcrystalline cellulose (MCC) is one of the most commonly used fat mimetics in food products, thanks to its ability to simulate the functional properties of fats, such as the appropriate mouthfeel, consistency, firmness and structure. Its application is significant in confectionery and bakery products, frozen desserts, salad dressings, fillings, cheeses and spreads [4]. There are two types of microcrystalline cellulose, powdered MCC and colloidal MCC [5]. Powdered MCC is very good fat mimetic in products that have a reduced moisture content, for example, emulsion systems in confectionery products, such as biscuit fillings. It is most often used in combination with sugar syrups and in the amount of up to 15 % [6].

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Commercial colloidal microcrystalline cellulose is usually a mixture of MCC powder (cellulose gel) and Na–CMC (cellulose gum in amount of 8.5–15 %). Adequately dispersed cellulose crystals in a colloidal cellulose gel form a three–dimensional crosslinked structure, which is stable over a wide range of pH and temperature and which provides optimal functional properties of colloidal MCC. The viscosity of a colloidal microcrystalline cellulose suspension depends on various factors and generally it forms thixotropic gel. Various food products may contain colloidal MCC, such as low–fat products, dough, canned products, beverages, dairy and confectionery products, salad dressings, sauces [7].

The definition of appropriate components and their quantity is required for the formulation of a new food product. Besides that, the order of addition of raw materials is also very important in the aim to achieve desired product quality. Certain raw materials achieve their functional properties only in the adequate stage of production, or some components may reduce the functional properties of other components when they are added in inadequate phase of production.

Food products often contain additives, depending on their composition, in the aim to improve certain product properties. Additives are added to food products in the technological process of production, during preparation, processing, shaping or packaging [8]. According to technological criteria such as method and purpose of application during production, the additives can be classified into several groups: additives added during processing, canning additives, direct additives, indirect additives, mineral additives, nutritional additives, food coloring and other additives [9]. Preservatives ideally prevent microbiological spoilage of food. The preservative provides prolonged protection of food from subsequent spoilage after opening the package or when the package is not hermetically sealed. There are three basic types of preservatives used in food, antimicrobial preservatives, antioxidants and anti–browning agents.

Antimicrobial preservatives are used to control and prevent the growth of microorganisms in food products. According to the INS (International Numbering System for Food Additives) and E system of numerical labeling of additives, they were assigned by INS and E numbers from 200–290. Antioxidants are used to prevent the oxidation of lipids and/or vitamins in food products. The main role is to prevent self–oxidation, which is reflected in the development of rancidity and unpleasant odor and taste of food. In the system of numerical designation of additives, they are assigned by INS and E numbers from E 300–E 324. Antioxidants, can be natural substances, such as vitamin C (E 300) or vitamin E (E 306), or synthetically produced chemical substances, such as butyl–hydroxyanisole (BHA, E 320) and butyl–hydroxytoluene (BHT). Anti–browning agents are chemical substances that are used to prevent enzymatic and non–enzymatic browning of food products. The most commonly used are vitamin C (E 300), citric acid (E 330) and sodium sulfite (E 221) [10].

This work examines the influence of additives on the process of obtaining stable cellulose based fat mimetics. Applied additives affect to the durability of food products and increase their shelf life. Cellulose based fat mimetics play important role in substitution of fat in low energy food product, thus the influence of added additives on functional rheological and textural properties of the fat mimetic is examined in this work. By obtained results, the order of adding the raw materials during the production of low energy, or low fat, or reduced fat food products, which includes the application of cellulose based fat mimetics will be defined.

2. MATERIALS AND METHODS

2.1. Materials

During the experimental work was used cellulose based fat mimetic Vivapur MCG 611F manufactured by John Rettenmaier & Sönhe GMBH + CO, Rosenberg, Germany. The chemical composition of MCG 611F includes microcrystalline cellulose (MCC=81.2–88.7 %) and sodium carboxymethyl cellulose (NaCMC=11.3–18.8 %). The distilled water was used for the hydration of fat mimetic fibers. Also, the mixture of additives was applied and included sodium ascorbate E 301, trisodium citrate E 331 and sodium acetate E 262.

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2.2. Methods

2.2.1. Preparation of fat mimetics

The powder of the observed fat mimetic was dispersed in distilled water in concentrations of 5 and 10 %, as commonly used concentration for formation of cellulose gel systems. Separately were prepared the fat mimetics with same fiber concentrations, but with addition of additives. The mixture of additives was used and included 0.150 g of sodium ascorbate E301, 0.150 g of trisodium citrate E331 and 0.200 g of sodium acetate E262 per 100 g of cellulose gel. The dispersed systems were prepared by a homogenizer (Ultra Turrax T–25, IKA Werke GmbH & Co, Germany), with S25 N–18G accessories using the rotation speed of 6500 rpm for 4 min. After preparation, the dispersions were kept at 4°C for 24 h to form a gel.

2.2.2. Rheological determination

Rheological properties of obtained fat mimetic gel systems were determined by rotational viscometer HAAKE RheoStress RS600 (Thermo Electron Corporation, Karlsruhe, Germany) with plate–plate sensor PP60 Ti (plate diameter was 60 mm and gap 1 mm). The measurements were done at 25±0.1°C. Flow properties were defined by hysteresis loop method and observing the shear stress (τ) over shear rate ($\dot{\gamma}$). The samples were exposed for 3 min to shear rate ramped up from 0–100 s^{-1}. The following 3 min the shear rate was constant at 100 s^{-1} and finally ramped down to 0 s^{-1} for 3 min.
Storage modulus (G') and loss modulus (G'') were defined by dynamic oscillatory measurements in the range of linear viscoelastic regime (LVE). The moduli were observed during increased frequency from 1 to 10 Hz and at constant shear stress of 1 Pa. The results were expressed as value Tan δ=G''/G' [11].
Viscoelastic response of the samples at constant stress, as well as their behaviour after removing the stress, were determined by creep & recovery analysis. The analysis was performed in the LVE regime in which the deformation amplitude was proportional to applied stress amplitude. The creep time with constant stress (σ=1 Pa) was 150 s and the recovery period after removing the stress was 450 s. Creep data, collected under constant stress (σ) over time (t), can be described by a creep compliance (J) function, in terms of shear deformation (γ), using equation (1).

$$J(t) = \gamma(t)/\sigma \quad (1)$$

The linear development of compliance as a function of time is imitated by mechanical model with several springs (elastic contribution) and dashpots (viscous contribution) [12]. Mathematically, the relationship between elastic and viscous properties can be simulated by Burger's model that is combination of Kelvin model (consisting of a spring and dashpot connected in parallel to each other) and Maxwell model (consisting of a spring and dashpot connected in series to each other) placed in series.
The creep data were analysed by Burger's model presented by equation (2):

$$J(t) = J_0 + J_1 \cdot (1 - \exp(-t/\lambda)) + t/\eta_0 \quad (2)$$

For the recovery phase the equation of the Burger's model is equation (3):

$$J(t) = J_{max} - J_0 - J_1 \cdot (1 - \exp(-t/\lambda)) \quad (3)$$

The value J_0 is the instantaneous compliance, J_1 is retarded (viscoelastic) compliance, J_{max} is maximum compliance, λ is mean retardation time and η_0 is Newtonian viscosity [13, 14]. The part of the curve that describes the recovery of the system can be described by the proportions of elastic (J_e) and viscous (J_v) deformations in the maximum compliance of the system. There is a relative elastic part J_e/J_{max} [%] (part of

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the structure that recovered after removing the stress) and relative viscosity part J_v/J_{max} [%] (part of the structure that did not recover after removing the stress, lost amount of deformation) [15].

2.2.3. Determination of textural characteristics

Textural characteristics were determined using a Texture Analyzer TA.HD Plus, Stable Micro Systems. A specific method *Comparison of the consistencies by back extrusion* was used and performed by Back extrusion cell (A/BE) kit, which contains a base for positioning the sample, a plexiglass sample vessel with an inner diameter of 50 mm and a compression disk with a diameter of 35 mm. A 5 kg measuring cell was used. During the measurement, the sensor disk penetrates 30 mm through the sample, after which it returns to the starting position. The parameters of the method are: moving speed before analysis 1 mm/s, during analysis 1 mm/s, returning speed 10 mm/s, distance 30 mm and contact force 10 g. The firmness of the gel system is described by maximum realized force during the penetration of the disk at a distance of 30 mm. The consistency of the gel system is defined by the size of the surface that the obtained curve builds with the abscissa. The negative part of the graph was obtained during the return of the measuring disk through the sample and describes the flow resistance that the sample exhibits. The cohesiveness of the sample is defined by the negative maximum on the graph, and the area that the curve of the negative part of the graph builds with the abscissa represents the viscosity index (Fig. 1) [16].

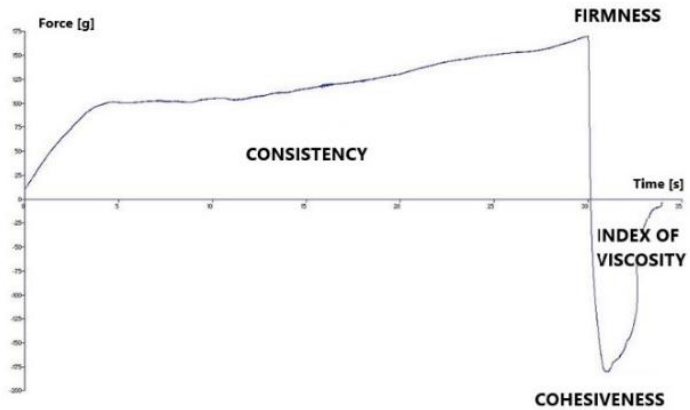

Figure 1. Typical curve of textural properties for gel

3. RESULTS AND DISCUSSION

3.1. Rheological characteristics of fat mimetics

3.1.1. Flow curves of MCG fat mimetics without and with added additives

The rheological behavior of observed MCG 611F fat mimetics and the obtained flow curves are shown at Fig. 2. The influence of increased fibers concentration in the fat mimetics gel, from 5 to 10 %, as well as the influence of addition of additives mixture on flow curves were observed.

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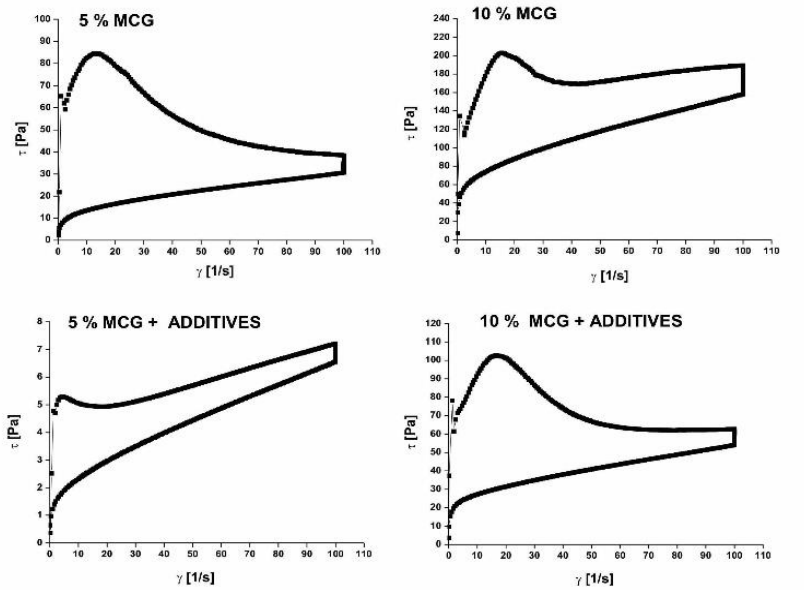

Figure 2. Flow curves of MCG 611F fat mimetics with different fibers concentrations and with addition of additives mixture

A common characteristic of all shown flow curves for MCG 611F fat mimetics is thixotropic type of flow, that pointed to the viscoelastic structure of the system. The obtained curves formed a specific hysteresis loop during the increasing and decreasing shear rate phases. The strength of the structure of the rheological system can be assumed based on the appearance and surface of the hysteresis loop. When the shear rate increases, the internal structure is destroyed, and when the shear rate decreases, the rheological system is structured and recovered. In the presence of weak secondary linkages, the structure is easily destroyed, and this is manifested by a small area of the hysteresis loop. Therefore, the larger surface area indicates the complex structure of the rheological system, as well as the possibility of significant changes in the structure during the shear stress action [17].

Such rheological behavior of MCG fat mimetics is a consequence of the nature of MCG fibers that consist this fat mimetic. Microcrystalline cellulose fibers are very easily interconnected, due to their pronounced ability to hydrate and to increase in volume in the aqueous medium. That generally leads to crosslinking and the formation of a three–dimensional gel structure [18]. As the concentration of MCG fibers increases, the degree of crosslinking also increases, which caused the strengthening of the gel structure and reflected in a significant increase in the value of the hysteresis loop area. Rheological parameters that describe presented flow curves are the value of the hysteresis loop area A_0, yield stress τ_0, critical shear rate $\dot{\gamma}_c$ and critical shear stress τ_c (Tab. 1).

Table 1. Rheological parameters of flow curves for MCG 611F fat mimetics with different fibers concentrations, without and with the addition of additives

MCG gel composition	Rheological parameters of flow curves			
	$\tau_0 \pm$ SD [Pa]	$\tau_c \pm$ SD [Pa]	$\dot{\gamma}_c \pm$ SD [1/s]	$A_0 \pm$ SD [Pa/s]
5 % MCG	2.19 ± 0.01	79.43 ± 7.02	13.16 ± 0.24	2909.00 ± 62.45
5% MCG+ADDITIVES	0.37 ± 0.02	5.30 ± 0.25	4.63 ± 0.06	149.31 ± 6.99
10 % MCG	7.20 ± 0.50	208.37 ± 26.44	19.16 ± 1.99	6717.33 ± 567.71
10% MCG+ADDITIVES	3.64 ± 0.09	102.64 ± 9.22	16.99 ± 0.15	3369.00 ± 26.31

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Yield stress τ_0 is the minimum value of shear stress needed for the system to begin to flow [19]. The ascending curves of MCG gels at critical shear rates ($\dot{\gamma}_c$) and at critical shear stresses (τ_c) had a peak, which indicated to the destruction of their structure after which the system flows freely. The values of the critical shear rate and critical shear stress increased with increasing concentration of MCG fibers in the system. Also, there is an increase in the value of the yield stress, which pointed to the initial resistance of system to flow, as well as an increase in the area of the hysteresis loop with increasing fibers concentration.

A significant decrease in all observed rheological parameters can be observed for the flow curves of MCG gels in which formation the additives were included. The most noticeable decrease in the value of hysteresis loop area was for 5 % gel with added additives, compared to 5 % MCG gel without the additives. Also, the value of hysteresis loop area was reduced for 10 % MCG gel under the influence of additives addition, but in a lesser extent (Fig. 2). This observation was confirmed by the parameters of flow curves presented at Tab. 1. The area of the hysteresis loop of 5 % MCG gel which contained additives decreased for 94.87 % compared to the area of the hysteresis loop of 5 % MCG gel without additives. For 10 % MCG gel this reduction in the hysteresis loop area was for 49.85 % compared to 10 % MCG gel without additives. The values of all other observed rheological parameters were also significantly reduced with the addition of additives into the gel structure (Tab. 1). Reduction of critical shear rates and critical shear stresses with addition of additives indicated to the presence of much weaker bonds in the gel system with additives and obtained systems are very susceptible to stress and easily break down compared to gels without additives.

The inclusion of selected additives in the structure of MCG gel resulted in significant decrease in the strength and stability of the system and a sudden decrease in the consistency of the gel. An important feature of all observed gel systems is that regardless of the addition of additives, these gels retained the thixotropic flow properties and an ability to form a hysteresis loop. Additionally, gels with 10 % of MCG fibers and additives had stronger and more stable structure than gels with 5 % of these fibers and additives.

3.1.2. Viscoelastic properties of fat mimetics without and with the addition of additives

The viscoelastic behavior of the observed fat mimetics was defined by dynamic oscillatory measurements and creep & recovery test. Both types of measurements were performed in a linear viscoelastic regime at stress values that do not have a destructive effect on the system structure. Fig. 3 shows the results of dynamic oscillatory measurements in the region of linear viscoelastic regime.

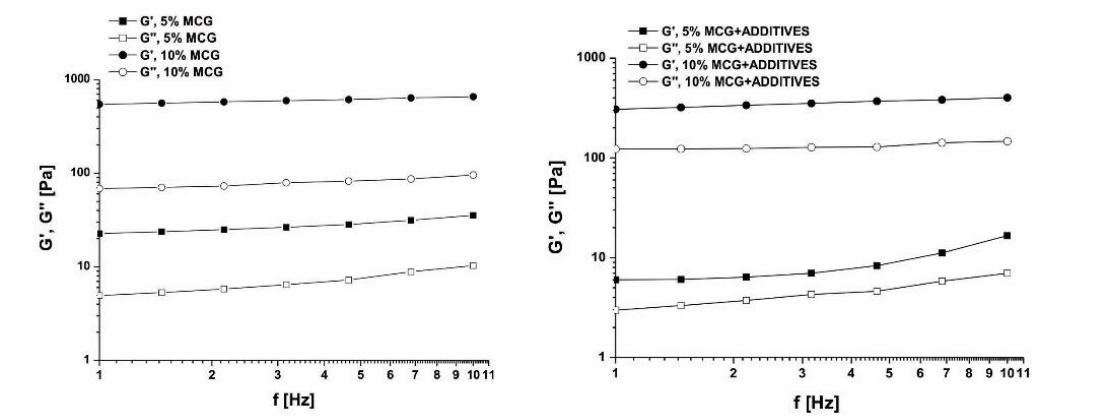

Figure 3. Changes of storage G'and loss G" modulus with increasing frequency for MCG gels without and with additives

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For all observed systems it was characteristic that storage and loss modulus increased with increasing frequency. Also, the storage modulus G' was always higher than loss modulus G", in the range of applied frequencies. Such viscoelastic behavior is typical for concentrated systems in which the cross–linked gel structure is formed [19].
An additional parameter that describes the viscoelastic nature of the system is Tan δ. This rheological parameter is defined as the ratio G"/G' and represents a measure of the relative magnitude of the viscous and elastic parts of the system. The lower the values of Tan δ, the nature of the system is more elastic [20].
Since the observed MCG gels had the higher storage modulus G' than the loss modulus G", thus it was normal for their ratio or value of Tan δ to be less than one. The values of this viscoelastic parameter for all observed gel systems were ranged from 0.133 to 0.533, as shown in Fig. 4. Also, the values of the Tan δ parameter for fat mimetics without and with the addition of additives are shown in Fig. 4.

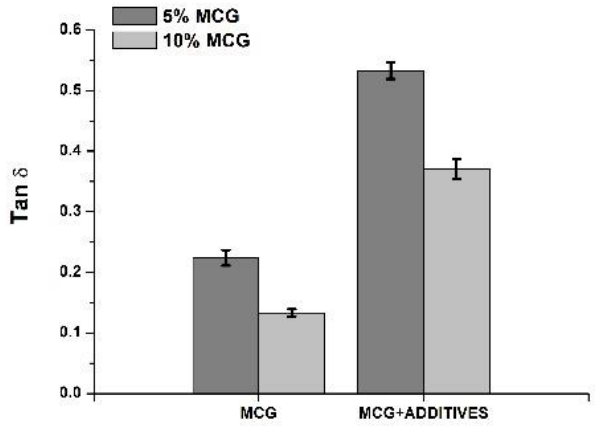

Figure 4. Tan δ for MCG fat mimetics depending on fibers concentration and presence of additives

As it was already mentioned, lower values of the parameter Tan δ indicate a firmer and stronger gel structure. That means larger amount of bonds with elastic nature, which contribute to a firmer consistency of the system and confirm a stronger structure. It can be seen from Fig. 4 that the values of Tan δ for gels with additives, regardless of the gel concentration, are always higher than Tan δ for gels without additives. Based on this, it can be concluded that the presence of additives significantly reduces the number of possible bonds with elastic nature and to some extent reduces the degree of crosslinking in the system. This is certainly due to the size of the additive molecules, which are very small compared to the macromolecules of fibers fat mimetics, and which are fitted in the macromolecules interspace. Also, the polarity of these small additives molecules certainly prevents the interaction between the fibers and the polar water molecules. This leads to a decrease in the degree of hydration of fiber macromolecules, to a decrease in their activity and degree of crosslinking.
According to the decreasing values of Tan δ, it is noticeable that gels with higher fibers concentration, regardless of the presence of additives, are always with more elastic nature and stronger structure than gels with 5 % of fibers. Amount of 10 % of MCG fibers in the system instead of 5 % reduced the value of Tan δ for 40.62 %. While the application of additives during formation of MCG gel increased the values of Tan δ for 137,95 % and for 178,95 % compared to gels without additives in the structure. It means that additives have the greatest influence on obtaining a weak elastic structure of gels.
The viscoelastic properties of gel systems during the action of constant stress are additionally defined by creep & recovery curves. The intermolecular bonds of the sample are stretched during the influence of

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constant stress. The initial compliance of the system (J_0) is related to the initial elastic deformations, and the subsequent compliance of the system (J_1) to the viscoelastic deformations. This phase is described by the first part of creep & recovery curve and it is called the creep phase. The creep phase is followed by a recovery phase, in which there is no influence of stress and the balance between the intermolecular bonds is established, thus the system is partially recovered from the influence of stress. The resistance of viscoelastic materials to the influence of constant stress is usually nonlinear and the permanent deformation of these systems is usually less than the total deformation applied to the system, due to their ability to attain recover of significant part of the structure with stored energy [12, 14]. Creep & recovery curves of fat mimetics without and with the addition of additives are shown in Fig. 5.

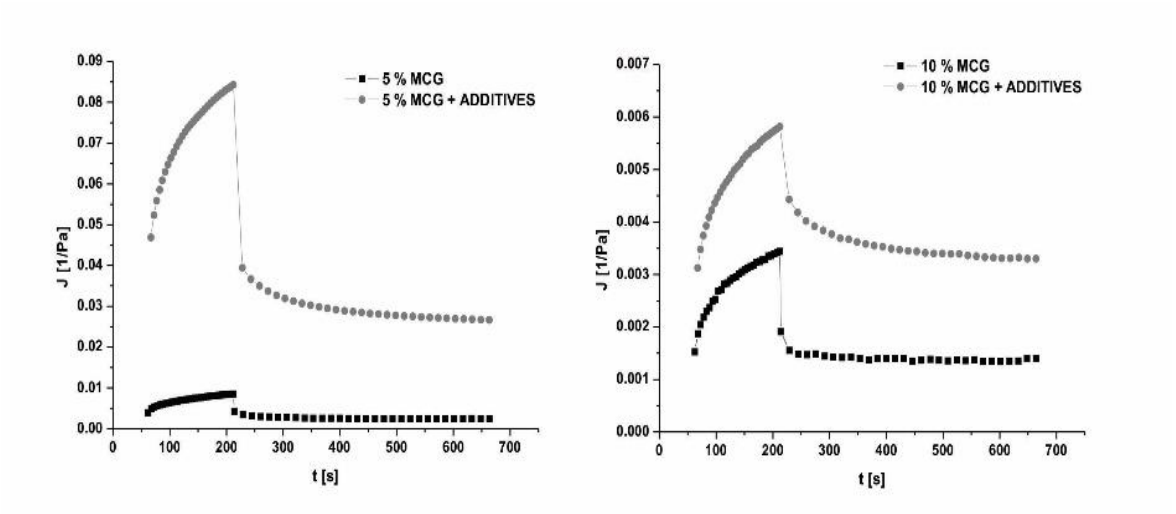

Figure 5. Creep & recovery curves of MCG gels with and without additives

Increasing concentration of fibers in the fat mimetic decreased the compliance of the system (J) during the constant stress, which means that the gel system with 10 % of MCG fibers provided greater resistance to deformation. This is contributed by more intensive crosslinking at high fibers concentration, which strengthening gel consistency and increases the stability of the gel structure. Addition of additives during the formation of gels caused pronounced increase in compliance of all fat mimetics, compared to fat mimetics without additives.

Thus, the application of additives during gel formation significantly reduced the ability of system to resist the influence of stress and the system is more susceptible to deformation due to weak connection of the structure and poor consistency. All obtained creep & recovery curves were well fitted to the equations of the Burger's model, which is confirmed by high coefficient of determination, r >0.99. Characteristic parameters of the creep & recovery curves influenced by increase in the fibers concentration in the gel and the application of additives are shown in Tab. 2.

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Table 2. Parameters of the Burger's model for creep & recovery curves of MCG gels with and without additives

MCG gel composition	Creep phase					
	$J_0 \pm SD \cdot 10^3$ [1/Pa]	$J_1 \pm SD \cdot 10^3$ [1/Pa]	$\eta_0 \pm SD \cdot 10^3$ [Pas]	$\lambda_1 \pm SD$ [s]	$J_{max} \pm SD$ [1/Pa]	
5% MCG	4.38 ± 0.49	2.99 ± 0.21	23.53 ± 1.58	92.33 ± 0.01	9.05 ± 0.62	
5% MCG + ADDITIVES	46.91 ± 0.21	27.81 ± 0.08	2.52 ± 11.30	92.20 ± 0.04	84.27 ± 1.55	
10% MCG	1.45 ± 0.07	1.14 ± 0.008	61.35 ± 0.41	92.45 ± 0.04	3.30 ± 0.06	
10% MCG + ADDITIVES	3.13 ± 0.09	1.92 ± 0.06	36.53 ± 1.48	92.37 ± 0.02	5.82 ± 0.03	
	Recovery phase					
	$J_0 \pm SD \cdot 10^3$ [1/Pa]	$J_1 \pm SD \cdot 10^3$ [1/Pa]	$\eta_0 \pm SD \cdot 10^3$ [Pas]	$\lambda_1 \pm SD$ [s]	$J_e/J_{max} \pm SD$ [%]	$J_v/J_{max} \pm SD$ [%]
5% MCG	4.77 ± 0.65	1.07 ± 0.06	24.03 ± 1.31	288.50 ± 0.10	64.77 ± 0.64	35.25 ± 0.62
5% MCG + ADDITIVES	39.49 ± 2.46	8.80 ± 0.05	15.85 ± 0.41	288.33 ± 0.05	68.33 ± 0.62	31.67 ± 0.60
10% MCG	2.05 ± 0.12	0.61 ± 0.15	41.05 ± 5.99	288.57 ± 0.06	61.87 ± 0.81	38.13 ± 0.81
10% MCG + ADDITIVES	2.43 ± 0.02	0.83 ± 0.01	12.22 ± 1.11	288.50 ± 0.01	77.71 ± 0.20	22.29 ± 0.23

The observed fat mimetics during the influence of constant stress provide certain resistance and exhibit creep properties. During the recovery phase, the observed systems showed significant ability to recover their structure. Observing the viscosity of fat mimetics, an increase in the viscosity with the increase of the fibers concentration was noticed. That was expected, due to more intensive crosslinking and stronger gel structure of fat mimetics with 10 % of fibers. However, in the presence of additives this degree of crosslinking is significantly lower and the viscosity of all gel systems with additives is significantly lower than in gel systems without additives. During creep phase the viscosity decreased with the addition of additives for 40.46 and for 89.29 %, while during the recovery phase the viscosity decreased for 34,04 and for 70,23 %. Consequently, the values of the compliance parameters (J_0, J_1 and J_{max}) increased, indicating to a decreased system resistance to the applied stress, due to the weakening of its structure. The changes of all these creep & recovery parameters showed in Tab. 2 confirmed the results of the previous rheological determination of the observed gel systems. Also, in all obtained gels the amount of elastic bonds, value J_e/J_{max}, is always higher than the amount of viscous bonds, value J_v/J_{max}, during the recovery phase of the system. That means that all observed gels are still with dominantly elastic semi–solid structure, which is more or less weakened depending on their composition and the presence of additives. The amount of these bonds is in accordance with the viscoelastic parameter Tan δ for all observed gels.

3.2. Textural properties of fat mimetics without and with additives

Viscoelastic properties of gel food systems are analyzed at small deformations and under conditions which do not disturbed the gel structure. But, industrial processes, as well as the application of gels, often require high stresses. Therefore, large deformation tests, such as textural determinations are very useful for characterizing of gel systems. Textural methods are based on the deformation of the sample to the point of permanent structural change [21]. The firmness and consistency of gel are closely related textural parameters, which are determined by the penetration of the sensor element through the gel. The parameters that describe the cohesiveness and viscosity are determined during the return of the sensor element through the gel sample and are related to the resistance that the system provides. Increasing the concentration of fibers in observed gels of fat mimetic led to an increase in the firmness and gel consistency. The absolute values of the gel viscosity and cohesiveness index also increased with increasing fibers concentration in the gel (Tab. 3).

Table 3. Textural parameters of MCG fat mimetics without and with additives

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MCG gel composition	Firmness $F_1 \pm SD$ [g]	Consistency $A_1 \pm SD$ [gs]	Cohesiveness $F_2 \pm SD$ [g]	Index of viscosity $A_2 \pm SD$ [gs]
5 % MCG	110.11 ± 8.62	2383.77 ± 663.32	-90.93 ± 4.10	-190.48 ± 5.91
5 % MCG+ADDITIVES	20.57 ± 0.09	412.75 ± 1.96	-15.59 ± 0.07	-1.14 ± 0.01
10 % MCG	343.68 ± 51.54	7766.73 ± 990.12	-361.16 ± 25.52	-818.10 ± 21.94
10 % MCG+ADDITIVES	134.39 ± 13.09	2939.99 ± 485.83	-115.31 ± 15.83	-251.39 ± 28.00

Increasing the fibers concentration in observed gels of MCG fat mimetic certainly contributed to increase in the texture parameters, which indicated to stronger consistency, greater strength, system viscosity and connectivity of components. Those results of textural determination confirmed previously determined rheological parameters of the gels without additives (Tab. 3). But, the textural properties of fat mimetic gels were significantly changed with the application of additives during formation of the gels, and all textural parameters were reduced. The firmness of MCG gel decreased for 81.32 % and for 60.90 % with addition of additives compared to MCG gels without additives. All other observed textural parameters also decreased with application of additives. The presence of small polar molecules of additives, such as applied ascorbates, citrates and acetates, certainly has a negative effect on the process of fibers hydration and the crosslinking process, and thus on the formation of a stable crosslinked gel structure [22].

4. CONCLUSIONS

Cellulose fibers of observed fat mimetic have a pronounced hydration and molecular interaction ability, which provide intensive crosslinking and formation of three–dimensional gel structure. With the increase of the fibers concentration in the system, the degree of crosslinking is larger, and thus the strength of the gel structure and its consistency. Small molecules of additives, which have also hydrophilic nature, interfere with hydration and physically prevent crosslinking. Because of that structural interactions in the hydrated mixture of cellulose fibers of MCG fat mimetic and additives, the rheological and functional properties of obtained gel are reduced, pointing to lower degree of crosslinking and the decreased stability of obtained gel structures. The obtained results indicate that the application of additives in a mixture with MCG fat mimetic fibers during hydration is undesirable. Additives cannot be used before or during the hydration of fat mimetic gels, because of their negative influence on gel formation. In order to ensure obtaining of stable, cross–linked gel of fat mimetic with adequate rheological, textural and functional properties, the mixture of additives is added in subsequent stages of low–fat food products production.

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SEMIAUTOMATIC AND FULLY FUNCTIONAL ELECTROCHEMICAL MICROANALYZER BO-05 SUITABLE FOR SCIENTIFIC, DIDACTIC AND ANALYTICAL APPLICATIONS: THE USE IN THE POTENTIOMETRIC ANALYSIS OF DRUGS

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ABSTRACT

This article presents the potentiometric method of determination of chlorides using the original BO-05 electrochemical microanalyzer. The quantification of chlorides is one of the frequently performed methods, both in the indirect determination of active pharmaceutical ingredients (API) and impurities in pharmaceutical raw materials, pharmacopoeial substances or pharmaceutical formulations as well. Successfully validated method was used to the analysis of chlorides in the preparations containing verapamil hydrochloride in form of tablets Staveran® and Verapamil®. The mean content of the studied API calculated to one tablet was close to the declared and equal to 123.6±1.5 mg and 122.6±1.1 mg, respectively. The presence of excipients have no significant impact on the final results. Thus shown that the electrochemical microanalyzer BO-05 is suitable for scientific, didactic and analytical applications.

Keywords: potentiometric methods, potentiometric titration, electrochemical microanalyzer, verapamil hydrochloride

1. INTRODUCTION

The BO-05 microanalyzer combines both the functions of a potentiometer with high internal resistance and a potentiostat. The innovative BO-05 analyzer was constructed with the use of electronic devices and programmed appropriately for analytical purposes, using various types of sensors and microsensors, both scientific and educational. The analysis includes such methods as: potentiometry, stripping potentiometry, linear sweep voltammetry, anodic stripping voltammetry or chronoamperometry. The constructed microanalyzer is connected to a computer *via* the R-232 port which allows the manual and automatic control. Both the software and the equipment used minimize the amount of data necessary for the correct performance of the analysis and enabling quick online presentation of results. Direct connection with MS Office Excel enables immediate analysis of the obtained results and significantly improves the necessary calculations.

Verapamil (2-(3,4-dimethoxyphenyl)-5-[2-(3,4-dimethoxyphenyl)ethyl-methylamino]-2-propan-2-ylpentanenitrile;hydrochloride – Fig. 1) is currently one of the most widely used anti-arrhythmic drugs from the group of calcium channel blockers [1-4]. In pharmaceutical preparations, such as Staveran® and Verapamil®, it is used in doses of 40, 80 or 120 mg.

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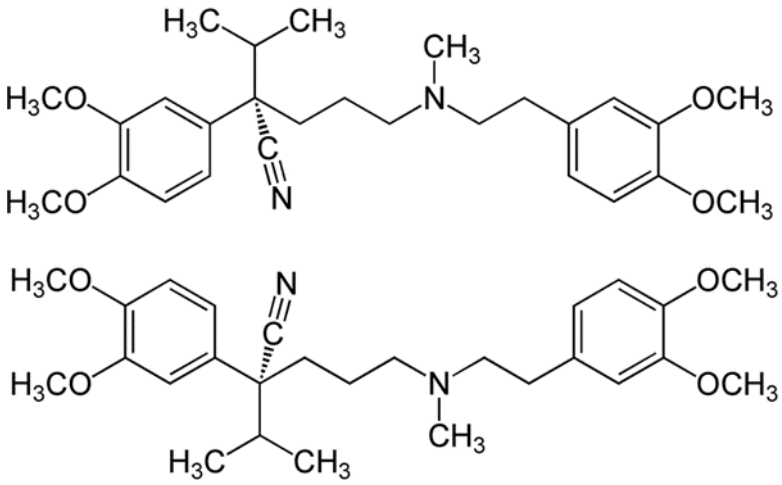

Figure1. The chemical structure of verapamil

Verapamil is determined by various analytical techniques e.g. chromatographic [5-8], spectrophotometric [1], spectrofluorometric [9,10], voltamperometric [11], amperometric [12]. Verapamil with hydrochloride, in the studied pharmaceutical preparations, is present in a molar ratio of 1:1 [7]. Therefore, it is possible to determine the content of verapamil based on the amount of chlorides in this preparation. To determine the chloride content, a precipitimetric method with a potentiometric end point detection was used. Standard solutions containing chlorides were titrated with silver nitrate(V) solution in the platinum electrode system as indicator and silver chloride electrode as reference. In this work, an attempt was made to indirectly determine the content of verapamil in the studied drugs, based on the analysis of the content of an equivalent amount of chlorides.

2. MATERIALS AND METHODS

2.1. Materials

Used in the research potassium nitrate (KNO_3) and concentrated nitric acid (HNO_3) were both Suprapur Merck. Water (quadruple-distilled) with a conductivity of less than 1 μS/cm was obtained using an S2-97A2 distillation apparatus (ChemLand, Stargard Szczecin, Poland). The Staveran® (Medana Pharma SA) and Verapamil® (Mylan Pharmaceuticals Inc.) drugs were obtained in a local pharmacy.

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2.2. Instrumentation

All potentiometric measurements were performed using a homemade BO-05 analyser (Fig. 2).

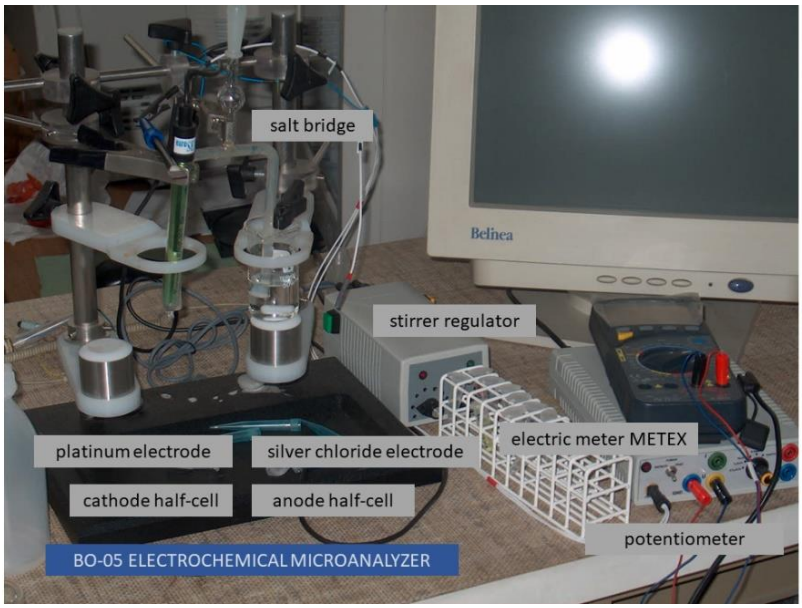

Figure 2. The image of the Electrochemical Microanalyser BO-05

The analyzer has been constructed using electronic components and programmed to be suitable for scientific, didactic and analytical applications using various electrochemical sensors and micro-sensors. The techniques accessible in the BO-05 analyzer include: various potentiometric methods, potentiometric stripping analysis, linear sweep voltammetry, anodic stripping voltammetry and chronoamperommetry. The input impedance for potentiometer was greater than 10^{15} ohms and the input current was lower than 0.1 pA. For driving potentiostat circuitry, potential range is ±8 V, 2 mV potential resolution and 10 ms timing template are typical working parameters. The work of the analyzer is controlled manually and communicated with the computer by the RS-232 port. The applied hardware and software arrangement minimizes number of necessary data interchange transactions during measurement procedure and enables a true on-line presentation of measurement results.

The presented system for electrochemical analyses consists of three separate hardware modules: the analyzer BO-05, a desktop or mobile computer and electrodes stand.

The block diagram of BO-05 analyzer is shown on Fig. 3.

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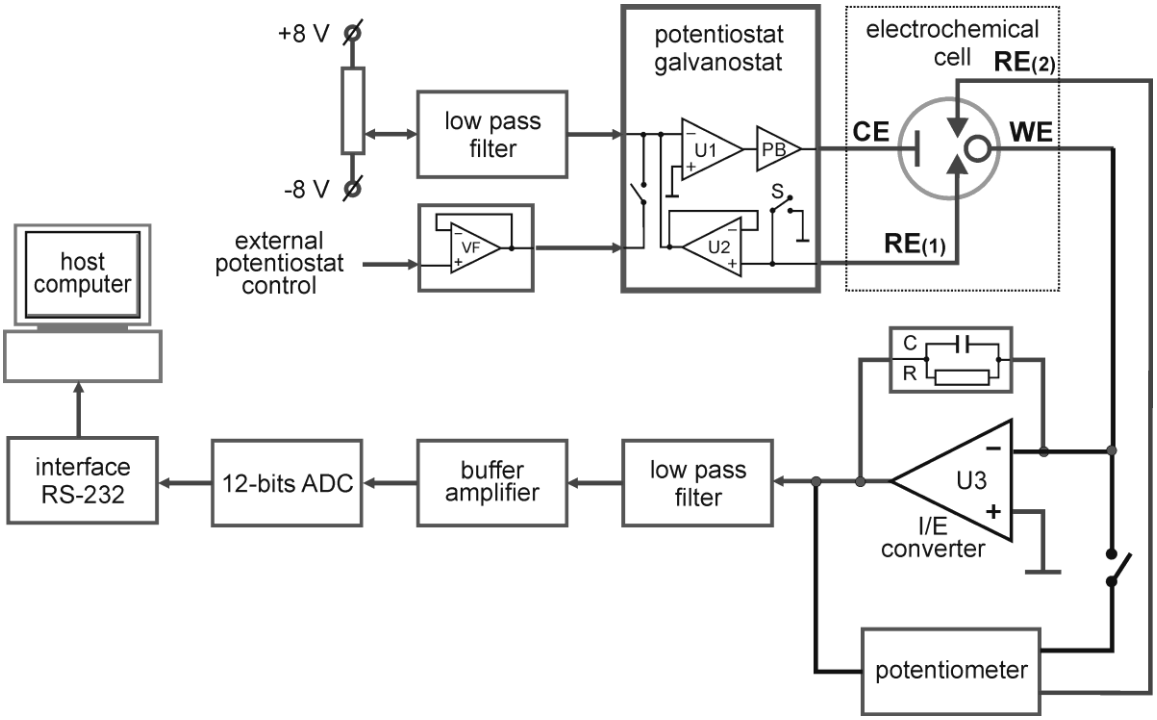

Figure 3. Block diagram of analyzer type BO-05. WE -working electrode; RE -reference electrode; CE -counter/auxiliary electrode; PB -power booster; VF -voltage follower; S -switch of potentiostat mode (two or three electrode)

The analyzer consists of the following functional subassemblies (modules): a) power supply, b) communication interface, c) analog to digital converters, d) potentiometer, e) potentiostat and current-to-voltage converter. Once measurement procedure is in progress the only data transmitted to host computer are results of analog to digital conversions and other data necessary to presentation of results in a form of measurement curve. The potential waveform, through low pass filter drives inverting input of summing, first amplifier of the potentiostat (U1). The output signal of the summing amplifier is than current-boosted (PB) and flows to counter/auxiliary electrode (CE) of electrochemical cell. Reference electrode (RE) and high input impedance amplifier (U2) close feedback loop of the potentiostat providing summing current without disturbing the potential of the reference electrode. Configuration switch (S) enables selection of potentiostat mode: two or three electrode. Feedback loop amplifier (U2) and reference electrode (RE) are used in three-electrode configuration only, while in two-electrode configuration, seldom used, counter electrode serves as quasi-reference electrode. The current that flows through working electrode (WE) as an effect of processes inside the electrochemical cell is further amplified in I/E converter (U3). Value of R and C elements in a feedback loop of I/E converter determine the instrument's sensitivity and are selected prior to measurement execution by configuration reed relay connectors. There are 5 full-scale ranges available from 10 nA to 10 mA, and they allow for precision adjust of the instrument's sensitivity with regard to the monitored process. An output low-pass filter is used to suppress high frequency noise generated (in analog circuitry, cell and cables) on ADC input. High performance amplifiers (AD744 by Analog Devices) are used in the analyzer's analog circuitry with exception of current booster (OPA627 by Burr Brown).

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2.3. Methods

Before starting the analysis, 20 tablets of the each preparation under study were weighed and ground in a porcelain mortar. The obtained powder was partially accurately weighed and transferred quantitatively to a 50 mL volumetric flask and filled to the mark with quadruple-distilled water. The resulting solution was filtered.
5 mL of 1 M KNO_3 was added to the first of the measuring cell, and an appropriate amount of the sample solution, 20 µl of concentrated HNO_3 and quadruple-distilled water were added to the second one measuring cell. Half-cells were connected with each other using an electrolytic key filled with 10% agar gel and 0.1 M KNO_3. 0.001 M $AgNO_3$ solution was added in equal portions to the measuring cell with the API under study at 10 s intervals. The SEM measurement of the measuring cell was recorded at 10 s intervals. Thus, 15 to 25 readings were obtained depending on the concentration of verapamil in the sample. The titration end point was determined automatically by the Hahn's method. The analyzes were performed in the Pt platinum electrode and Ag/AgCl silver chloride electrode.
The obtained results were developed with the use of a proprietary program Metex-bis, written in a Visual Basic. The statistical analysis was performed using the Statistica 10.0 program and the Microsoft Excel 2010 spreadsheet.

3. RESULTS

3.1. Method validation

3.1.1. Precision

To check the precision of the method at one level, stock solution containing chlorides was prepared. Then, 100 µL of this solution with 50 µL of concentrated nitric acid were added into the measuring cell and filled with quadruple-distilled water up to 5 mL. The chlorides content in analyzed samples calculated to verapamil hydrochloride was 0.8 µg – Tab. 1. Fig. 4 shows examples of titration curves.

Table 1. Results from method validation. Precision.

No	sample [µg]	calculated amount [µg]	$\bar{x}$	SD	%RSD
1	0.800	0.827	0.810	0.021	2.59
2		0.843			
3		0.809			
4		0.779			
5		0.816			
6		0.816			
7		0.786			
8		0.793			
9		0.822			

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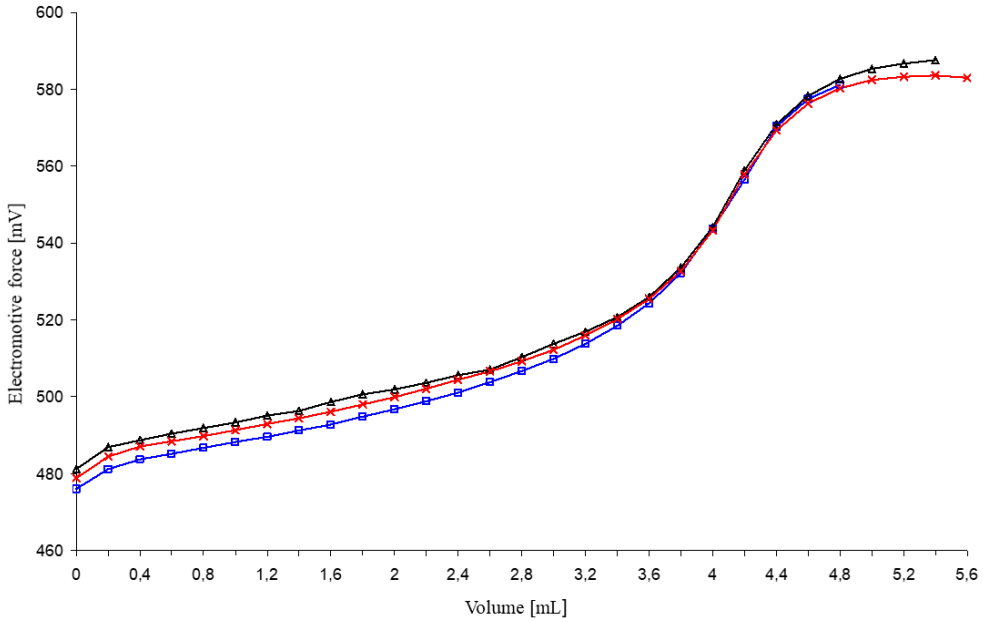

Figure 4. Examples of titration curves obtained for the same concentrations of standard chloride solutions

3.1.2. Linearity

To determine the linearity, 6 solutions at concentration in the range of 0.1 mmol/L - 1 mmol/L were prepared. The results were analyzed using the linear regression method. The regression equation and the correlation coefficient were as follows: y[V] = 0.1372+1.9857×c; R=0.9995.

3.1.3. Limit of detection and Limit of quantification

Using standard deviation and slope of a straight line coefficient. The values of LOD and LOQ were determined and equal to 0.1 μg and 0.32 μg respectively.

3.1.4. Specificity

Due to the similar properties of chlorides to iodides and bromides and the possibility of their presence next to each other. their influence on the end point of titration was investigated. The graph below shows the titration curves obtained for chlorides next to iodides and bromides. The method can be considered specific, because the PK values are clearly separable – Fig. 5.

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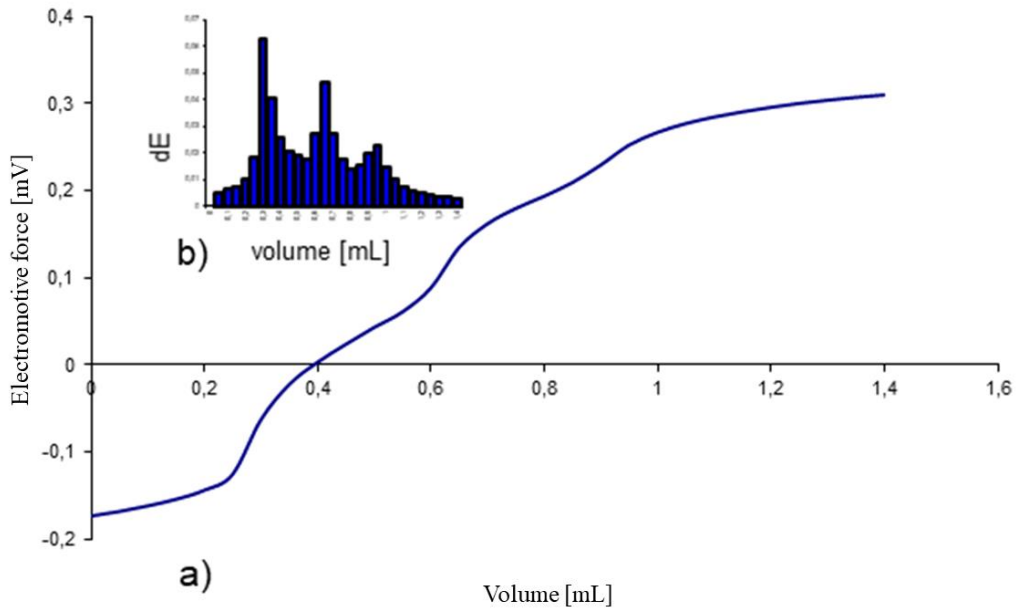

Figure 5. a) titration curve of chlorides in the presence of iodides and bromides; b) plot of the first derivative of the above determination

3.1.5. Accuracy

Recovery was calculated on the basis of determined content of verapamil hydrochloride to amount added to working solutions. The results are summarized in Tab. 2:

Table 2. The results of the recovery obtained for the Staveran® preparation and their statistical evaluation.

sample	% recovery	$\bar{x}$	SD	%RSD
1	99.65	99.78	1.98	1.98
2	99.63			
3	98.55			
4	103.68			
5	98.59			
6	98.60			

3.2. Analysis of pharmaceutical preparations

The pharmaceutical preparations of Verapamil® and Staveran® in the form of tablets were analyzed. The manufacturer's declared content of verapamil hydrochloride in each tablet is 120 mg. The obtained results of chlorides content in the weighted portion of prepared samples enabled to determine the content of verapamil in samples under study – Tab. 3. In the next step, the calculated amounts were converted into the average content of the active substance under study per 1 tablet of the pharmaceutical preparation of Verapamil® and Staveran® - Tab. 4.

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Table 3. The content of verapamil hydrochloride determined in samples under study.

weighted portion [mg]	declared content [mg]	determined average amount [mg]	SD	%RSD	n
613.2	309.0	315.8	12.8	4.06	6
604.4	304.6	318.4	12.7	4.00	6
605.3	305.0	318.2	9.6	3.00	6
849.7	298.26	307.3	4.7	1.52	6
850.7	298.61	311.1	5.2	1.66	6
782.0	274.50	289.2	6.5	1.68	6

Table 4. Calculated content of verapamil hydrochloride in preparations per 1 tablet of the pharmaceutical preparation Verapamil® and Staveran®.

pharmaceutical preparation	average amount per 1 tablet [mg]	SD	%RSD	n
Staveran® 120 mg	123.6	1.46	1.1	6
Verapamil® 120 mg	122.6	1.08	0.88	6

4. CONCLUSIONS

Due to the obtained results, it can be concluded that the analytical method using the BO-05 microanalyzer is an effective and reliable in the indirect determination of verapamil in selected pharmaceutical preparations. Under conditions of experiment, the method featured high sensitivity, good precision and comparability of results as proven by the method validation and statistical analysis of the results. The presence of excipients in the formulation have no significant impact on the results. Due to the low cost and relatively short duration of the analysis as well as the significant automation. This method can be proposed as comparable to other methods of determining of drugs.

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EFFECT OF DIFFERENT COMMERCIAL ENZYMES ON THE CLOTTING OF MILK AND CERTAIN PROPERTIES OF CURD

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ABSTRACT

More researches published data about the milk curd properties, evaluated the importance in the cheese making, but an analysis of importance of these properties in practical applications is usually lacking. We investigate the milk curd behaviour using different enzyme preparations at the cutting of curd. We focused on the well measurable properties as clotting time, viscosity of curd, texture properties and whey separation rate of cur at cutting time. Approximately five minutes difference was determined between the clotting times. Investigated the curd properties we found significant differences between the hardness on samples clotted with CHY MAX® M 1000 and NATUREN® Premium 145 enzymes. Other properties did not show significant differences, but in some case differences were remarkable. Discovered differences e.g. approx. 5% whey separation rate difference and the different trends of adhesive force and adhesiveness confirm that such studies should be carried out. Summarized effect of different enzymes can alter the cheese making technology significantly in practice. Considering every aspect, in our investigation the CHY MAX® M 1000 enzyme seemed the best.

Keywords: clotting enzymes, curd properties, cheese making, curd loss, syneresis,

1. INTRODUCTION

In many cases, the fundament of cheese making is the clotting of milk by enzyme. The clotting is performed by different enzyme preparation for splitting kappa-casein causing aggregation of casein micelles leads to the formation of protein network. For the curd formation, removing required amount of liquid phase (whey) is essential by, taking advantage of syneresis.

Conditions of clotting and syneresis determine the clotting time, curd properties, syneresis rate, losses in whey, etc., so the optimization of clotting and the handling of curd is a well discusses area. The preliminary cold storage, the pasteurization, the fat content, ionic Ca^{++} content of milk, as the clotting temperature and amount of clotting enzyme have significant effect on clotting time and the texture of curd, e.g. on hardness [1], [2], [3].

After the clotting, syneresis becomes to determining factor in whey separation. It is affected by temperature, elapsed time, pH, rheological properties of the gel at cutting, curd surface area, proteolytic activity of enzyme and $CaCl_2$ concentration [4], [5], [6], [7], [8].

Factors affecting syneresis rate and extent, including milk composition and pre-treatment, coagulation factors, rheological properties of the gel at cutting, curd surface area, external pressure, and curd temperature and pH, have been widely reviewed [4], [8], [5], [6], [7].

Many different empirical techniques have been published to study the kinetics of syneresis as reviewed by [8], [9]. First order kinetics has been reported by many authors to describe the rate of syneresis [4], [10], [11]. Preliminary techniques were developed for monitoring syneresis parallel with the moisture determination of curd, evaluated the changes of curd volume, and measuring the volume of separated whey from the curd [12], [4]. Some researcher worked using image analysis to monitor the curd shrinkage [13]. This was a very new type of non-destructive method, so it contained better information for practice. But we can say that because of the continuous changing of the structure of curd and the composition of curd during clotting and mainly during the curd handling, makes it very difficult to develop a good method for the

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precise and accurate monitoring [14]. Indeed, the experimental conditions are often too distant from industrial practice to extrapolate results.
Ultimately, curd properties and syneresis can determine the most important aspects of cheese making as sensory properties of cheeses and losses during the processing. Therefore, in last decades some empirical or instrumental methods were investigated for monitoring the syneresis during the "in-vat" processes of cheese making [9], [10], [13], [15], [11], [16]. After clotting, the cutting of curd is the first essential treatment can alter the curd loss dramatically. Too soft curd at the cutting leads more curd losses (affecting the cheese yield), retarded syneresis can result weak or deficient cheese sensory properties. However, the producers attach valuable information about the working of enzyme preparations, but different products with same certificate clotting activity usually do not lead to the same clotting time, curd strength and syneresis rate. The effect of different enzyme preparations on the mentioned consequences is not discussed sufficiently.
Due to the mentioned aspects we investigated the curd properties at the time of cutting. Three different commercial enzyme preparations were used in this experiment. Gel strength (viscosity), clotting time, other measurable texture properties and water binding capacity of curds were investigated in our work.

2. MATERIALS AND METHODS

2.1. Pre-treatment of raw cow milk

Cold stored raw cow milk was used for every measurements. Milk was standardized to 3.50 % (m/m) fat content and protein content range was 3.25-3.31 % (m/m). Milk analysis was performed by using of Bentley 150 milk analyser (Chaska, Minnesota, USA) at 40°C. Milk was pasteurized at 72 C° with 1 minute holding in a jar using induction heater then was cooled at 32 C° for the clotting. After cooling 0.02% $CaCl_2$ (with 30% solution) was added into cheese milk then it was agitated to ten minutes.

2.2 Enzymes

Three commercial enzyme preparations were used in this research. CHY-MAX® M 1000 (EC 3.4.23.4) pure chymosin produced by Aspergillus niger var. awamori, CHY-MAX® Plus: (EC 3.4.23.4), pure cattle chymosin (EC 3.4.23.4) produced by Aspergillus niger var. awamori and NATUREN® Premium 145 (EC 3.4.23.4) 83-88% calf chymosin and 12-17% cattle pepsin mixture. All enzymes were produced by Chr. Hansen Denmark.

Table 1: Enzyme parameters given in the producers' certificates

Enzyme preparation	Offered dosage [IMCU L^{-1} milk]	Average activity [IMCU mL^{-1} enzyme]
CHY-MAX® M 1000	20-50	1000
CHY-MAX® Plus	30-60	1200
NATUREN® Premium 145	30-60	1145

20 % (m/m) solutions were made with distilled water from every enzyme preparation and the dosage for investigations was based on the arithmetic mean of the offered dosages. Clotting was performed in water bath (Memmert WNB-14, Schwabach, Germany). Investigations to determine the clotting time and peak viscosity value of the clotting curve were performed in two replicates. There was no enough data to calculate standard deviation.

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2.3. Viscosity

Viscosity was measured with vibration viscometer (A&D SV-10, Japan). Data were fixed by using of the own software of instrument. Plastic cuvette was filled with 45 mL inoculated milk sample the sensor head of viscometer was immersed fully into the sample. Software fixed the temperature and viscosity of milk using 30 sec. sampling. The time-viscosity curves reached a peak in every case, and we considered the peak time as the cutting (clotting) time.

2.4. Texture investigation

Texture parameters were measured in five parallel samples in case of every enzyme preparations. After adding enzymes, samples were agitated for 1 minute, then were stored in water bath at 32°C for 30 minutes, thus the clotting was the same. Enzyme inoculations were performed with 10-minutes slides, thus giving enough time for the measure. Brookfield CT3 texture analyser was used for the investigation. Parameters as follow: cycles: 1, test type: penetration, target value: 20 mm, trigger load: 40 mN, probe: 25.4 mm diameter plastic piston, test speed: 0.5 mm/s. Hardness, hardness work, adhesive force and adhesiveness were used for the evaluation. The explanation of used parameters is shown in Fig 1. Five parallel measures were performed from every sample.

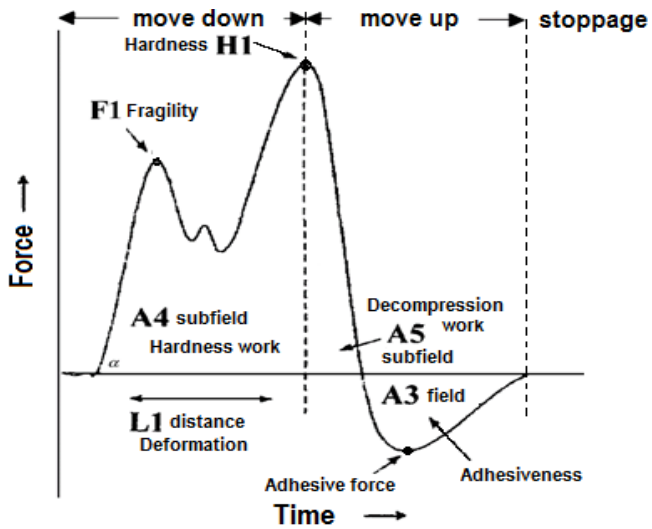

Figure 1: Explanation of different texture parameters (Armero and Collar 1997)

2.5. Water binding capacity

Gravimetric method was use for the determination of water binding capacity of curds. Pre-treatment of milk was same as mentioned before. After the enzyme addition the weight of samples in 100 mL plastic centrifuge tubes was determined to four decimal places. Clotting times at 32°C was set considering the result coming from the viscosity measures (peak times of different samples). After the clotting we cut the curds to eight vertical parts and centrifuged the samples at 5000 rpm for 5 minutes in an MPW 350 (MPW Med. instruments Warsaw, Poland). Then whey was separated and weights were measured to for decimal places. Result was expressed in percentage of separated whey from curd. Five parallel sample were investigated from every sample.

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3. RESULTS AND DISCUSSION

3.1. Viscosity – clotting time

The evolution of time-viscosity curves was very similar, but we explored differences in the maximum values of viscosity and time associated with them (Fig 2).

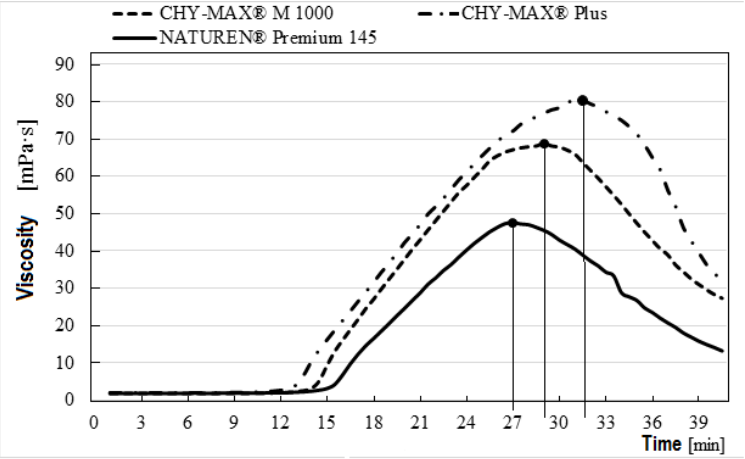

Figure 2: Viscosity development of curds clotted with different enzymes as a function of time (average of two replicates)

Samples needed different time for reaching the peak of viscosity (considering as clotting time). We recorded approximately 5 minutes difference between samples clotted with Naturen and Chy-Max plus. The question is whether we can consider this as important difference in the cheese making technology.

Well, five minutes difference, mainly after the reaching an appropriate curd texture, doesn't seem important. The curd is hard enough, and there is no visible whey separation on the surface of curd. But considering the rate of syneresis after the clotting we can say, it can be. The rate of syneresis determines the speed of whey separation and thus, the residence time of curd in the cheese vat, during which fermentation takes place.

The optimal properties of cheeses depend on the complex physical and biological phenomena during cheese making so if the optimal balance changes, it can have a significant effect on the composition and sensory properties of cheeses. The fine structure of protein network formed during the clotting could modify the behaviour of curd and properties of cheeses.

Thus, we divided the time-viscosity curd to different stages, see Fig. 3.

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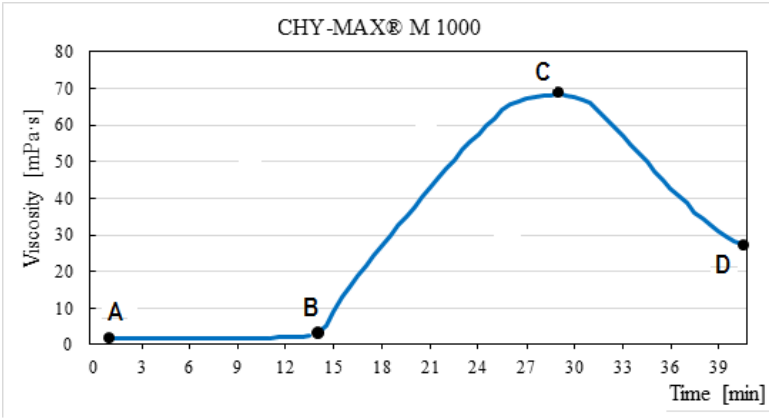

Figure 3: Different stages of clotting in our investigation (A. Enzymes inoculation; AB: preliminary casein micelle aggregation; B: at this moment the viscosity 75% higher than the initial one; B-C: clotting; C: cutting time of the curd considered at peak-time)

We explored different time for preliminary micelle aggregation using different enzymes. Because of the degree of micelle aggregation can alter the size of aggregate particle this can lead different fine structure of protein network, altering the clotting time and behaviour of curd.
We explored that the time needed for the different clotting stages and the ratio of stages were different in case of clotting by different enzymes (Tab. 2).

Table 2: the time required for different stages of clotting and ratio of them (average of two replicetes)

Enzyme preparations	AB [min]	BC [min]	AB/BC ratio	C [min]	AB/C ratio
CHY-MAX® Plus	12,0	18,5	165%	31,5	38%
CHY-MAX® M 1000	13,0	15,0	187%	29,0	45%
NATUREN® Premium 145	14,5	11,5	126%	27,0	54%

There was no remarkable difference in duration of micelle aggregation (AB) but likely the mentioned mechanism an activity difference of enzymes caused interesting variation in the time interval of milk gel formation period (BC). Data prove that the Naturen 145 enzyme (calf and cattle chimosyn mixture) caused the shortest "gelation" time while CHY-MAX Plus had the longest gelation period. It suggests that activity of biochemical reactions (as Ca bridges formation between micelles) modified by different enzyme types, can alter the cheese vat time and properties of curd.

3.2. Texture properties

Hardness

Second important aspect is the hardness of curd at the cutting. If we cut the curd before the optimal status, it leads significant more curd fines in whey causing more protein losses, but if we cut it too late, the syneresis becomes retarded can lead too high acidity of curd. We recognized remarkable differences in curd viscosity at cutting time. Sample clotted by CHY-MAX plus had hardness (viscosity) of about twice that of the sample clotted by Naturen Premium 145 (Fig. 4) and the difference was significant at $p<0.05$.

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The harder curd is better for cheese making, limiting the curd loss, but only up to a limit by our opinion. We recognized this difference with our naked eyes too. This variation can cause difference in the amount of curd fines in whey. These finding were interesting because of it is well known that the activity (concentration) and specific proteolytic ability of different enzymes coming from different origin (as chimosin, pepsin and microbial enzymes) have effect on the clotting time and sometimes on curd properties [2], [11], [3].

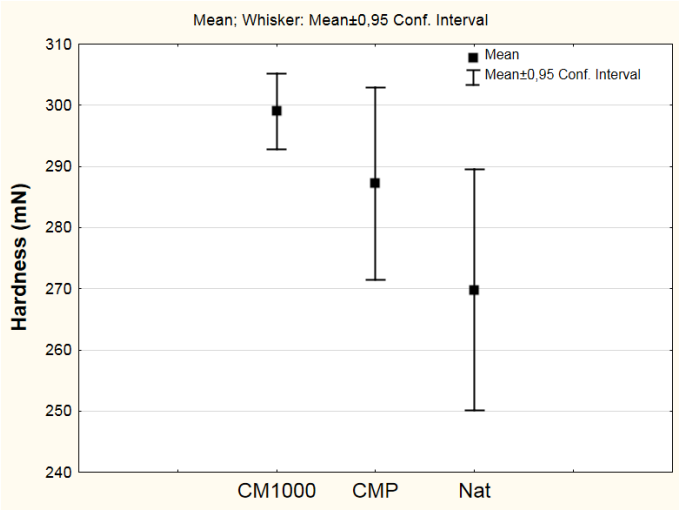

Figure 4: Curd hardness at cutting time (peak-time) as a function used clotting enzymes (CM1000: CHY MAX® M 1000; CMP: CHY MAX® Plus ; Nat: NATUREN® Premium 145)

But two enzymes used were produced by microorganisms. Furthermore clotting enzymes made from cattle or calf stomach usually have higher activity and better effect on the clotting. Whether there is a real, significant effect of a 5 min difference on the cheese making technology and on the properties cheeses made with the clotting by enzymes, requires further experiments.

Adhesive force

The adhesive force on the knives during cutting may be important because the higher force the higher ratio of curd fines can lead to more curd losses. Compared to those found for hardness, the adhesion force shows opposite trend for different enzymes, as shown in Fig. 5. Explored difference of means was not as high as in case hardness values.
Similarly, there was no significant difference in Adhesiveness values, although the means represented remarkable difference. It can be explained with the very wide confidential interval and high SD. We have to note that perhaps it would have been better to use another probe to determine the texture properties. The shape of probe may have been responsible for big difference between the values of parallel samples and for very high SD values.

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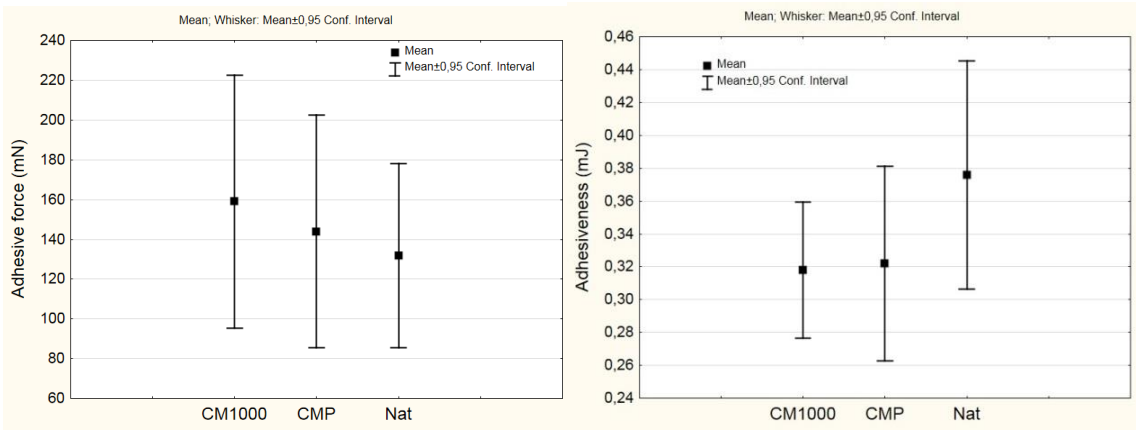

Figure 5: Curd adhesive force and adhesiveness at cutting time (peak-time) as a function used clotting enzymes (CM1000: CHY MAX® M 1000; CMP: CHY MAX® Plus ; Nat: NATUREN® Premium 145)

These high values also pointed that the cheese curd is very sensitive against to mechanical treatments so cutting and handling of curd is essential considering the curd loss. The curd properties are essentials in this term but the cutting and mixer frame design, distance of cutting knives, the material quality and the optimal setting of tool's speed are also very important for limiting the curd loss.

3.3 Water binding capacity

Water binding capacity of curd at cutting until the heating of curd basically determines the whey separation rate and the time requirement of "drying of curd". During this time period, lower water binding capacity is advantageous for prevention of over-acidification of curd that can lead to too low pH of cheese, altering the required sensory properties. We used the offered optimal amount of enzymes and conditions for clotting, but surprisingly, we explored different whey separation rates (Fig. 6).

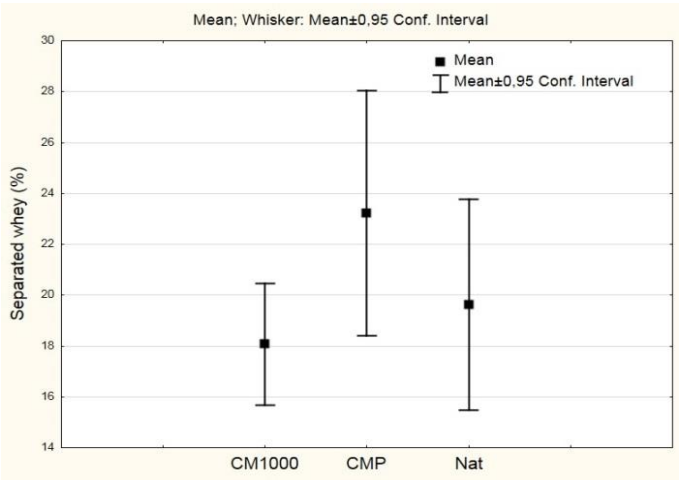

Figure 6: The degree of whey separation at cutting time as a function used clotting enzymes (CM1000: CHY MAX® M 1000; CMP: CHY MAX® Plus ; Nat: NATUREN® Premium 145)

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However, the differences were not significant, based on our method and measure, the difference of means were remarkable, by our opinion. In this examination CHY MAX® Plus enzyme had the highest and CHY MAX® M 1000 enzyme had the lowest whey separation rate. In other words, water binding capacity of sample clotted with CHY MAX® M 1000 was the most disadvantageous, considering the demand of fast whey separation.

4. CONCLUSIONS

Based on our method, the clotting time of milk samples using different enzymes showed differences. A five minute difference doesn't seem big, though it may be important considering the changes of curd properties and the behaviour of curd during the further cheese making steps.
All type of clotting enzyme was suitable for clotting of milk and to reach suitable curd properties. We did not determine extreme values during experiments. But, considering the deeper investigation of curd properties at cutting, we explored interesting differences cause by different clotting enzymes. Using the producer's suggestions for clotting, CHY MAX® Plus presented the highest and NATUREN® Premium 145 the lowest curd viscosity at cutting. Furthermore, the degree of milk (or curd) solidification was the lowest in case of NATUREN® Premium 145 samples.
Using texture analyser, explored differences of data coming from clotting with NATUREN® Premium 145 were confirmed, and significant difference was determined between the hardness means of NATUREN® Premium 145 and CHY MAX® M 1000 samples. In case of adhesive force and adhesiveness there were no significant differences, but we determined opposite trend between this two parameters, that is, greater adhesive force results in less adhesiveness. We also could not detect a significant difference in whey separation rate, but detected 4-5 percentage difference can lead significant time requirements in cheese vats to reach the optimal curd condition before removing it from vats for further curd handling.
Summarizing the explored differences we can say, these findings suggest that the behavior of curd may be different when different enzymes are used. At last, without the modification of technology and parameters, it can cause economical and product quality problems in cheese making.

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THE INFLUENCE OF PET AND PBT CONTAMINATION DURING TRANSPORTATION FUEL PRODUCTION VIA PYROLYSIS

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ABSTRACT

The pyrolysis of plastic waste is a promising method to reduce waste accumulation while it could provide value-added transportation fuels. The main goal of this study is to investigate the influence of PET and PBT contamination during plastic pyrolysis oil production utilizing HDPE, LDPE, PP, and PS mixtures as these plastics are good candidates for transportation fuel production via pyrolysis and distillation. Seven different waste blends were prepared and pyrolyzed in a laboratory-scale batch reactor equipped with reflux. Mass balance, gas analysis, thermogravimetric analysis, and deposit formation were evaluated. It was concluded that by increasing the PET or PBT concentration in the initial solid waste mixtures, the oil production decreases while the amount of gases increases. Additionally, either PET or PBT generates operational difficulties due to they form deposits in piping system in form of benzoic acid. The maximum concentration of these plastic waste materials was 20% (PET) and 25% (PBT) in this study as further increase blocked the cross-section of piping, causing operational difficulties. Based on the obtained results the concentration of PET and PBT should be limited in waste mixtures when transportation fuel production is desired.

Keywords: Plastic waste, pyrolysis, reflux temperature

1. INTRODUCTION

Pyrolysis of plastic wastes is a promising method to reduce environmental waste accumulation and could provide value-added transportation fuels. Although the influencing factors of plastic waste pyrolysis were investigated by several researchers, such as temperature [1, 2], pressure [3], time [1, 4], type of reactor [5, 6], catalyst [7, 8, 9], or plastic waste material used [5, 10], there is still a need for deeper investigation of the pyrolysis process. The influence of different contaminations plays an important role in present researches as not all the plastic waste types are suitable for high quality pyrolysis oil production. HDPE, LDPE, PP, and PS provide excellent pyrolysis oils [11] while they are present in global waste streams more than 50%. PET also contributes a significant amount to plastic waste, but it does not provide pyrolysis oil suitable for transportation. Additionally, PET can easily cause operational difficulties during a pyrolysis process, which is unfavourable. One of the main products during PET pyrolysis is benzoic acid [12] forming solid products at ambient conditions. Thus, PET can easily form solid deposits in low-temperature piping systems while oil is not produced. Zero percent liquid product was also presented in the case of PET pyrolysis in another study [13]. PBT has a very similar molecular structure compared to PET, and thus it behaves similarly during a pyrolysis process; however, very limited information is available describing plastic mixtures containing PBT. It can be stated in both cases that the pyrolysis of these plastics is challenging, but, on the other side, they can be present in waste streams even when they are virtually separated. Additionally, it is expected that the behaviour of PET and PBT in a pyrolysis system might be similar, as minor differences could be seen in molecular structures.

The main goal of this paper is to investigate the influence of PET and PBT contamination on the pyrolysis process when HDPE, LDPE, PP, and PS mixtures are used as these four plastics could generate excellent fuels (through pyrolysis and distillation) with properties close to the traditional gasoline.

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2. MATERIALS AND METHODS

The pyrolysis runs were performed in a laboratory-scale batch reactor equipped with reflux. The vapours exiting the reflux are condensed in a water-cooled heat exchanger, and the liquid product (pyrolysis oil) is collected in a product container at room temperature. The remaining gases were collected in a sample bag and flared after the measurements. Fig. 1 shows the schematic illustration of the measurement system.
The plastic waste recipes used in this study are summarized in Table 1. Each plastic waste blend contains five different plastic types separately gathered from local waste streams, and only the plastics with clearly visible identification codes were utilized. LDPE, HDPE, PP, and PS is present in each blend with a ratio representing the typical plastic demand in Hungary in 2018. 200 g solid waste blend was loaded into the reactor in each case, then the reactor was flushed with argon before measurement to eliminate the air from the system. The heat-up procedure started after the argon flush, and the pyrolysis runs were typically stopped when the temperature inside the reactor reached ≈520 °C as the cracking reactions ended by this temperature. It is worth noting that the PBT waste contained 15% glass fiber based on the identification code found on the surface of the material.

The pyrolysis gas was collected in a plastic sampling bag, and the composition was analyzed using gas chromatography (model: Dani Master; TCD detector with 3 columns: Restek RT-Q-Bond 30 m, 0.32 mm ID, 10 µm, Restek RT-Q-Bond 15 m, 0.53 mm ID, 20 µm and Restek RT-Msieve 5A 30 m, 0.53 mm ID, 50 µm; FID detector with 1 column: Rt-Alumina BOND/Na2SO4 30 m, 0.53 mm ID, 10 µm).

Table 1. Plastic waste recipes utilized for PET and PBT contamination analysis

	Concentration, %(m/m)					
Name	LDPE	HDPE	PP	PS	PET	PBT
PET-5	20.9	14.25	46.55	13.3	5	-
PET-10	19.8	13.5	44.1	12.6	10	-
PET-20	17.6	12	39.2	11.2	20	-
PBT-5	20.9	14.25	46.55	13.3	-	5
PBT-10	19.8	13.5	44.1	12.6	-	10
PBT-20	17.6	12	39.2	11.2	-	20
PBT-25	16.5	11.25	36.75	10.5	-	25

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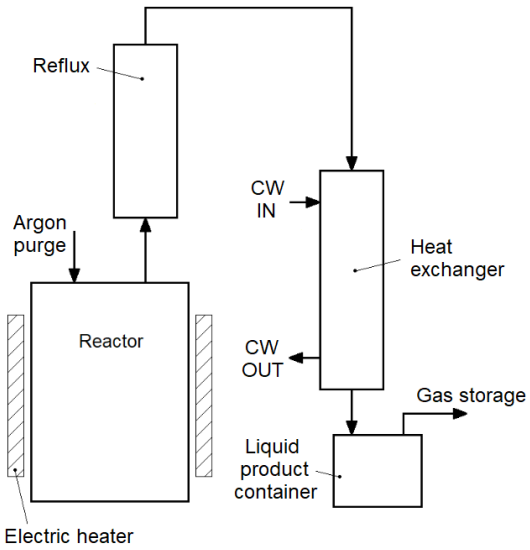

Figure 1. Schematic illustration of the measurement system

3. RESULTS

The mass distribution of the products during the pyrolysis runs is summarized in Table 2. Based on the obtained results, it can be stated that either PET or PBT significantly impacts the different products, which can be elucidated with the behaviour of pure materials during the pyrolysis runs. Based on a previous study [11], the neat PET generates 23.6% char and 76.2% gas, while less than 5% char and less than 40% gas might be generated in the cases of LDPE, HDPE, PP, and PS. This is supported by the TG analysis of materials used in this study (Fig. 2). It can be stated that high oil production can be reached when using LDPE, HDPE, PP, and PS plastic waste materials either in pure or mixed form. Thus, the addition of PET decreases the oil yield and increases the gas and char yield during the pyrolysis process. The same trends can be seen in the case of PBT contamination. It can be concluded that by increasing either PET or PBT in plastic wastes, the oil production decreases, while the gas and char production increases. This effect is not beneficial when oil production is the primary goal. Additionally, PET and PBT form benzoic acid, which is in the solid phase at ambient conditions. Thus, the benzoic acid can easily form deposits during pyrolysis runs with intensive cooling, such as during transportation fuel production via pyrolysis. The deposits were investigated in the system used in this study as well, Fig. 3 and Fig. 4 depict the actual status after each run. The thickness of the deposit increases by increasing the PET or PBT contamination; thus, a concentration limit was determined. Typically, the amount of solid deposit found in the heat exchanger after each run was slightly higher in the case of PBT. It was found that if the PET concentration is higher than 20%, then operational difficulties rise up while the oil quality significantly drops. The same in the case of PBT is 25%. Blending PET or PBT in higher concentrations is possible, but operational adjustments or system redesign is necessary, which can handle the above-mentioned deposit formation problems.

Table 2. Mass distribution of pyrolysis products utilizing various plastic waste mixtures

	PET-5	PET-10	PET-20	PBT-5	PBT-10	PBT-20	PBT-25
Oil, m/m%	77,6	70,55	63,3	76,85	73,6	63,75	59,8
Char, m/m%	6,6	7,15	7,55	4,3	5,45	7,55	10,5

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Solid deposits in heat exchanger, m/m%	0,2	0,4	0,15	0,65	0,95	0,75	0,5
Gas*, m/m%	16,1	21,9	29	18,2	20	27,95	29,2

*by difference

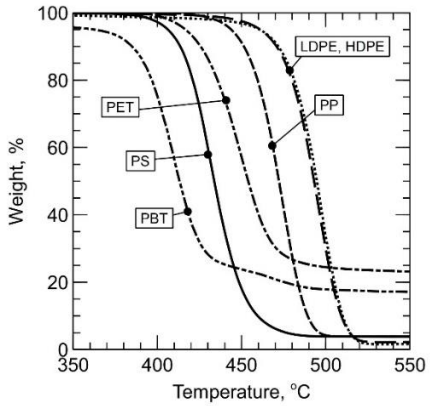

Figure 2. TG analysis of neat plastic wastes used in this study. MOM Derivatograph C/PC was used for measurements with a heating rate of 10 °C/min in a nitrogen atmosphere. The temperature is narrowed to a range of 350-550 °C for better illustration

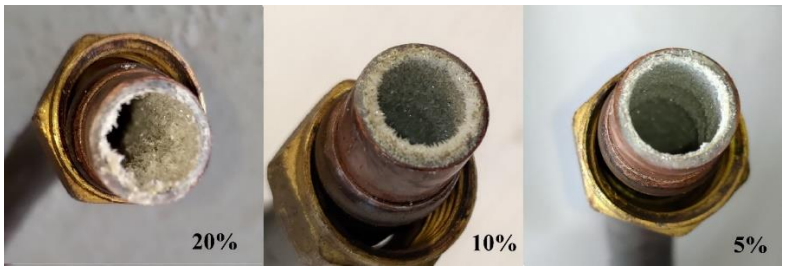

Figure 3. Deposit formation in case of PET

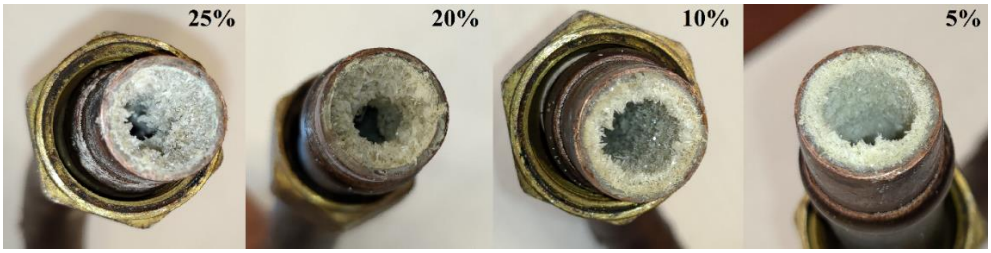

Figure 4. Deposit formation in case of PBT

The composition of the generated pyrolysis gas was measured by gas chromatography. The total hydrocarbon content of the gases is shown in Fig. 5. Generally, the hydrocarbon concentration decreases by increasing either the PET or PBT concentration of the initial solid blend, which can be elucidated with the fact that PET and PBT form mostly CO and CO_2 during a pyrolysis process due to the presence of oxygen atoms in the molecular structure. These oxygen atoms could partly or fully oxidize the carbon content. Additionally, PBT generates more hydrocarbons compared to PET as the presence of butylene in

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PBT adds more hydrocarbons to the pyrolysis gas. The hydrocarbons are mainly C1-C4 group alkanes and alkenes. The concentration of CO and CO_2 among with two selected hydrocarbons (C_2H_6 and C_3H_8) are depicted in Fig. 6. The CO and CO_2 increases, while the C_2H_6 and C_3H_6 decreases by increasing either the PET or PBT concentration. Generally, more CO and CO_2 were present in the gas phase during PET pyrolysis. As CO and CO_2 lower the heating value of the hydrocarbon-rich pyrolysis gas, PET and PBT contaminations are not beneficial in this context.

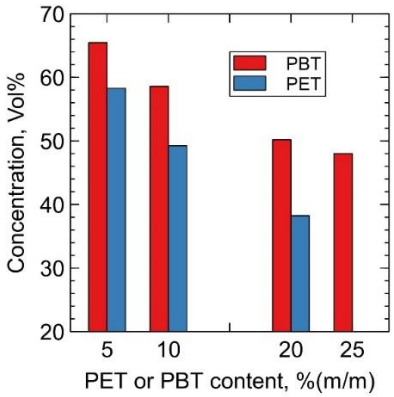

Figure 5. Total hydrocarbon content of the pyrolysis gas under various PET and PBT concentrations

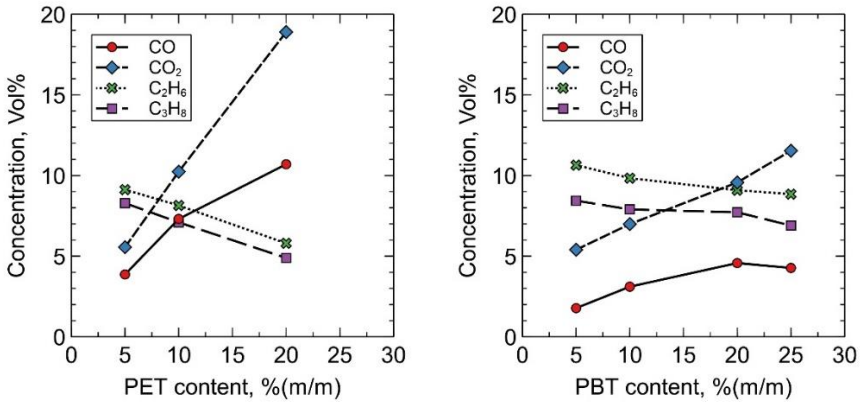

Figure 6. CO, CO_2, C_2H_6, and C_3H_8 content of the pyrolysis gas under various PET and PBT concentrations

4. CONCLUSIONS

The influence of PET and PBT contamination during the pyrolysis of HDPE, LDPE, PP, and PS plastic waste mixtures was investigated. Generally, the amount of pyrolysis oils decreased by increasing either PET or PBT in the initial solid material, while the amount of pyrolysis gases and solid residues increased. Additionally, the total hydrocarbon content decreased with PET/PBT increase, which is not beneficial from a heating value point of view. Solid deposits formed on the surfaces of heat exchanger piping and caused operational problems at higher concentrations; thus, the concentration of PET/PBT should be limited during the pyrolysis process. Overall, either PET or PBT is not beneficial when transportation fuel production is the primary goal of a pyrolysis process, and therefore pre-separation of these materials is necessary.

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THE MYSTERIES OF FINANCIAL CULTURE AND FINANCIAL HABITS

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ABSTRACT

In this research we will investigate the financial culture among the students of the Technical Faculty of University of Szeged. We will analyse the results of questionnaires about the students' financial culture and financial habits. We aim to learn more about the student's financial knowledge, debit card usage, savings and loan habits. Also, our research how the students' demographic and social background impact their financial decisions and habits. The results highlight that the respondents mainly seek financial advice from their family regarding financial decisions. Their financial behaviour is based on their communication with their parents and family background. Furthermore, the results show that the majority of the respondents have savings and are concerned about their future. We did not find any significant differences between gender, both genders equally have long-term savings. Generally, the respondents keep their savings in bank accounts or in cash, stocks or investing is not typical. We drew the conclusion that the students tend to refuse to take out personal loans and are risk-adverse in this matter. Finally, the students use their debit card widely and in their day-to-day life without the intention of influencing others.

Keywords: financial culture, financial attitude, financial habits, debit card, consciousness, long term savings

1. INTRODUCTION

Our financial culture and how we spend our money is one of the most important aspect of our life, as these financial decisions and their consequences have an impact on all segments of our life, such as our future and our standard of living. Many 'local and international' researchers have examined this topic, how different generations are considering their financial culture and habits. This topic is still relevant [1] because the recent economic crash in 2008 had a great impact on the fiscal security in Hungary and since then there have been regular financial culture measurements. Following the economic crash, it became crucial to improve our financial literacy and personal money management. [2]. Béres et al. [3] highlight that people who are financially sound, non-indebted, creditworthy people are less risky for financial institutions.

In his research, József Csernák [4] examined the factors influencing the willingness to save and borrow. His research revealed that the willingness of the rural population to save and borrow is influenced by several factors (e.g., respondent's age, occupation, education, marital status, and household income) simultaneously.

Previous studies have shown that the most influential factor is household income, in contrast, in Csernák's [4] research, the opposite result was obtained. According to his study, income remained an important factor, yet not the strongest factor. The results of Csernák [4] also prove that the propensity to save and the financial culture are influenced by many factors.

It is in the common interest of all economic person to develop the financial culture, as negative financial events are easier to avoid for households and businesses with a higher financial culture. However, the success of financial literacy programs requires knowledge of the factors that influence people's financial literacy and behavior [5].

It is difficult to define the financial culture as it is a complex and varied definition, which has been defined by many authors, however, they have not created a universal definition to date [6].

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The concept of financial culture is one of the most frequently mentioned expressions of economic life, the importance of which is emphasized by many and the serious consequences of its general absence for society are often presented [7].

It is crucial to present the different definitions [8] as our research goal is to analyse the university students' financial culture.

After researching the relevant literature and sources [9] it is understandable that most authors define financial culture as the best use of financial information, information gathering, organization and comparison; and individual decision-making. Kovács et al. [9] also emphasises the importance of fiscal knowledge, attitude and calculating skills regarding this research topic.

It is worth noting the OECD [10] case study, published in 2012, measured financial culture as the definition as the combination of the following elements; consciousness, skills, attitudes, behaviours, these are essential factors in financial decision-making also helping to reach personal financial stability. This abstract attempts to shed a light on the complexity of financial culture with the various competing components.

In order to learn more about financial culture, it is essential to examine the topic of financial behaviour. Xiao et al [11] considers all human behaviours and actions regarding personal money and spending as financial behaviour. Many researchers have measured the relationship between financial behaviours and demographics. Furnham [12] came to the conclusion in relation to demographic factors, that women are less likely to have long-term financial goals. Gresham and Fontenot [13] also analysed this particular topic, that gender plays a role in the differing financial goals. In their results it is clear that women worry more about their financial situation and they also prefer better quality products and services.

Regarding the correlation between age and financial behaviour, Furnham [12] found that the older generation are more conscious about their future and they tend to save significantly more than the younger generation. For the younger generations, money is the symbol of power and influence, and they do not consider savings and security as essential.

Furnham [12] and Lynn [14] both found that the educational level plays a significant role in people's financial behaviour. People with lower education tend to have less knowledge of how to manage their money and they see money as an object of social influence. However, people with higher education are more aware of sales and discounts, and they are looking to gain advantage through financial opportunities. As per Furnham [12] people with lower income are more hesitant about financial related decisions and are may be misled by others over their money and using their money to influence others.

The analysis of the knowledge of financial sources are just as important as the analysis of the financial culture. Kovács et al. [9] thinks that in order to be able to examine a groups' financial culture we need to know their financial background and where they source their information. Financial information sources area sources where we gather information about financial decisions or we seek guidance from professional help.

In the above-mentioned source Kovács et al. [9] drew the following conclusion, that younger people tend to seek financial information from their family members, from educational resources, personal experiences and from online sources. Gróf et al. [15] conducted a research among university students in Miskolc college, which led to the conclusion that students mainly trust their parents and siblings when it comes to financial decisions. Not surprisingly online sources are just as important as the parental advice in these situations. Furthermore, in this research we learn that TV and newspaper articles are less important when it comes to influencing one's financial decision-making.

Zsótér [16] found the first source of information young adults seek plays a critical role in defining their financial decision-making. In this research it is obvious that young adults seek advice primarily from their fathers regarding student loan and current account preferences. However, in relation to savings, the students would seek information from their mother.

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Parents are the number one influence on their children's financial behaviours, their first financial lessons are so important as they learn how to make wise choices and to live financially fit adult lives. The children's financial concepts like saving and spending will define their financial future; their money attitude and money management. [17]
The above-mentioned research results lead us to believe that the family is the prime information resource for the younger generation, who because of their lack of experience and knowledge follow parental patterns and influences.

2. MATERIALS AND METHODS

In my research I have circulated a paper-based questionnaire among the full-time students of the Technical Faculty in University of Szeged. I have also had meetings and consultations with experienced professionals countrywide. The questionnaire was conducted and analysed in 2020, with 350 respondents.
The sampled data and result analysis was undertaken in Microsoft Excel and PSPP statistical program.
After removing the initial errors, we have had altogether 339 valid responses. The sample cannot be considered as' population representative but the quantity of the answers is large enough to draw conclusions about the students' financial habits and culture.
The paper-based questionnaire consists of 5 parts, where we used a mix of closed-ended questions and open-ended questions, and a 5 scales of Likert scale.
Our hypotises and research questions were based on a previous study by Zsótér Boglárka [16], whose study also focused on the students' financial culture and behaviour in 2015.
In the following section I will address the different parts of the questionnaire:

1. Analysis of financial habits and attitudes:

   The questions focused on the student's daily spending habits and highlights the respondents 'relationship with money and material goods.

2. Financial knowledge and financial situation related questions:

   In the second part of the survey the respondents scored their financial knowledge and financial situation comparing with other young students on a five-level scale. 1 meant the lowest score and 5 was the highest score.

3. Debit card preferences and personal loans:

   In this section the respondents answered questions regarding debit card preferences and personal loan questions.

4. Savings and information sources:

   In the next section we asked the respondents to answer savings and information gathering sources related questions. We were able to measure what percentage of the students have a financial plan, long-term savings, how they keep their money as well who is their main information source in a decision-making situation.

5. Personal questions:

   In the last section of this survey, we asked the respondents personal questions. Questions about their demographics and academic background were asked. In this part the respondents were asked sensitive questions, such as gender, income, study field and questions about financial issues in their family,

The results are presented with graphics [18] and also in the following publication by György Hampel.

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3. RESULTS AND DISCUSSION

3.1. The attributes of the student sample

In our research 61,9 percentage of the students (210 people) were men and 38,1percentage were women (129 people). Furthermore, 88 % of the respondents (300 students) were studying in a BSc course, 12 % (39 people) were MSc students. Also, we learnt from our research data that 49% of the students scored their financial knowledge average/ the same in comparison to their classmates, 36 % scored it slightly better, 9 % scored it much better than other students.
Only 6 % of the respondents answered that their financial knowledge is much worse than other people's. They scored their financial knowledge on a 5 level Likert scale with an average score of 3,35 (deviation 0,80) This result means a slightly better than average adjunction, with a high rate of deviation.

3.2. Analysis student's financial habits and attributes

We aim to learn more about the students' financial habits and attributes with 9 statements in our questionnaire, scoring 1 to 5. We used statistical analysis to measure the given answers. The lowest score (2,38) was the following answer „I am keeping a financial plan, I keep a budget of my outcomes and incomes", and the highest score (4,55) was the next statement „I always pay back any borrowed money". Furthermore, 37,2 % of the respondents agreed on the next hypotheses „I regularly and thoroughly check my financial state". The highest score associated with this reply „I chat with my family about my money situation". More than half of the questioned students (56%) found the following statement correct, that they always pay any outstanding bills on time. It is worth mentioning that 33 % of students had regular monthly savings, and 41 % also consider their future expenses and save for them. Most of the respondents have agreed that „I tend to achieve my financial goals" and „I use my money cautiously, considering my goals".

3.3. Students materialization

We used the above mentioned nine statements in our survey to measure the students' material thoughts, on a one to five scale. The respondents have given the following answers. Most of the students (29%) did not perceive a person more successful because of the value of their property or car. One of the success factors in life is considered to be gathering more material goods was not replicated by our respondents, also most of the students did not mind if their classmates owned more valuables. The majority of the respondents disagreed on the following statement „I like products that influences' have an impact on others**"**. We learnt from the research that most students were happier if they could afford more and own better-quality products. Despite this, the students believe they have everything required to be able to live an enjoyable life. The respondents had a mixed opinion on the following remark „It sometimes frustrates me that I cannot afford some goods, that I desire**"** but most of them (28%) had marked this neutrally.

3.4. Debit card usage habits and attitudes

In our research we discuss the debit card usage habits and account information. We learnt from the survey that the majority of the respondents (94%) have their own bank account, while only 4 % do not. Also, 95 % of the students own a personal debit card, most of have either 1 or 2 cards, while only 5 % of the respondents do not have a personal debit card. The data clearly identifies that the majority (36 % of the respondents) are using their card regularly every week, while 33 % of the students are using their debit cards on a daily basis. The following figure (Fig. 1) will illustrate our findings of different types of the students regular spending.

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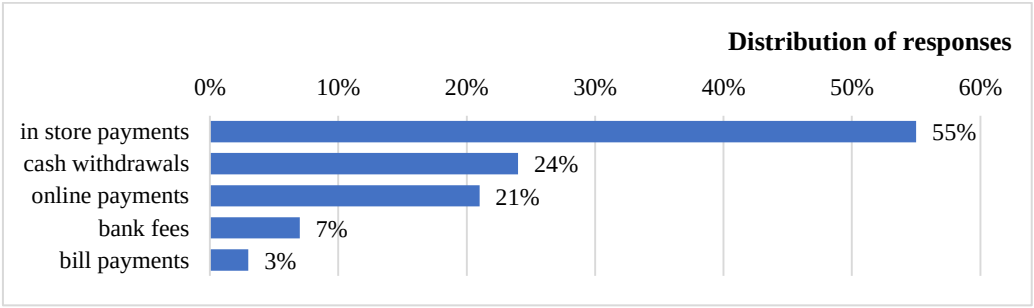

Figure 1. Most common debit card spending, Source: own work

As the above illustration shows the most popular mode of debit card use are still in-store purchases and cash withdrawals. It is worth mentioning that the less common type of spending was bill payment, because of the fact that their parents may be still the main bill payer.

3.5. Personal saving habits and loan willingness

After analysing the data, it is obvious that 84 % of the respondents have saved money and only 16 % do not have any forms of personal savings. The majority of female respondents (84,5 %) and male respondents (84,3 %) possess personal savings. The students of the Engineering Faculty mainly keep their savings in a savings bank account or at home in cash. Investments are not preferred in this research group; this can be considered as a risk-adverse behaviour. I have implemented 4 statements in order to examine the student's savings related attributes. After undertaking quality data analysis, it is clear that 11 % totally agree, and 25 % agree with the next statement „Money is there to be spent (consumed)", while 39 % marked this neutrally.
Furthermore, „I live for today, do not worry about the tomorrow" statement was strongly disagreed between the respondents. 73 % of the answers scored this as disagree. With the „Savings are crucial" statement and „We need to save for worse times" the students had a mixed opinion, 50 % totally agree with this and 38 % rather agree with this hypothesis.

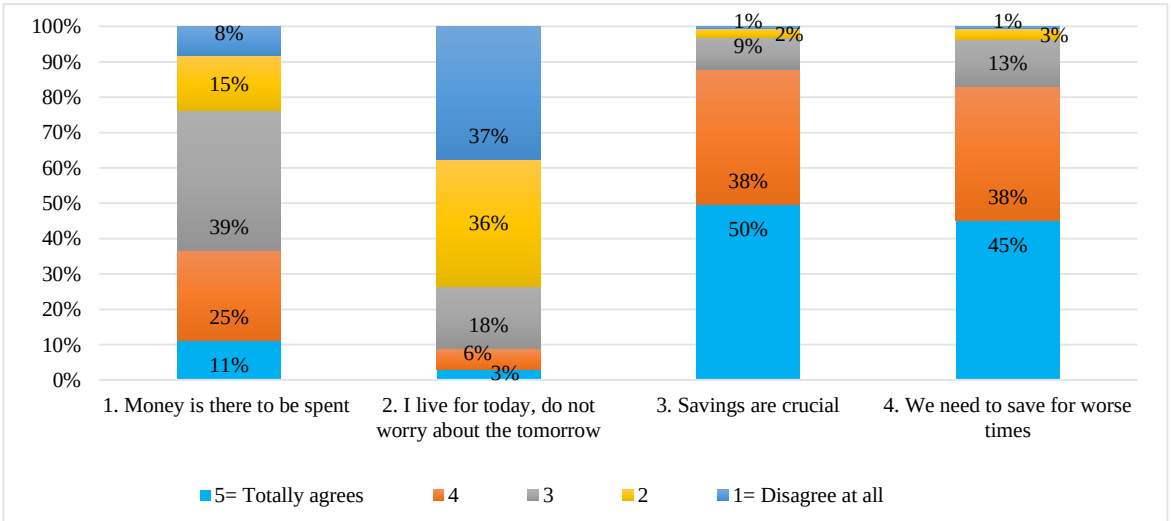

Figure 2. The student's relationship with savings, Source: own work

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Moreover, we found in our research that 90% of the students did not take a student loan and 4 % plan to take out in the future and 6 % already have a student loan. The 1. Figure represents the high cost of banking services, 7 %, in spite of that 90 % of the respondents did not take out a loan. This can be explained by their savings accounts' monthly maintenance fee and withdrawal fee.
Additionally, we have examined if the savings and student loans have a correlation to the individual's' monthly income rate. We have used a chi square distribution table to measure the variants and we found out that there is no correlation between the individuals' monthly income and their loan willingness. In relation to the question whether the students' saving rate is being influenced by their university studies (for example, undertaking a finance course) we have used a Pearson's chi-squared test. We learnt from this test that there is a significant relationship between the two variants, and completing a finance course can greatly benefit our long-term savings.

3.6. Information gathering and family communication

We have highlighted in our research the information gathering topic, who the students consider as their primary source of information in financial decision-making and in choosing products and services.

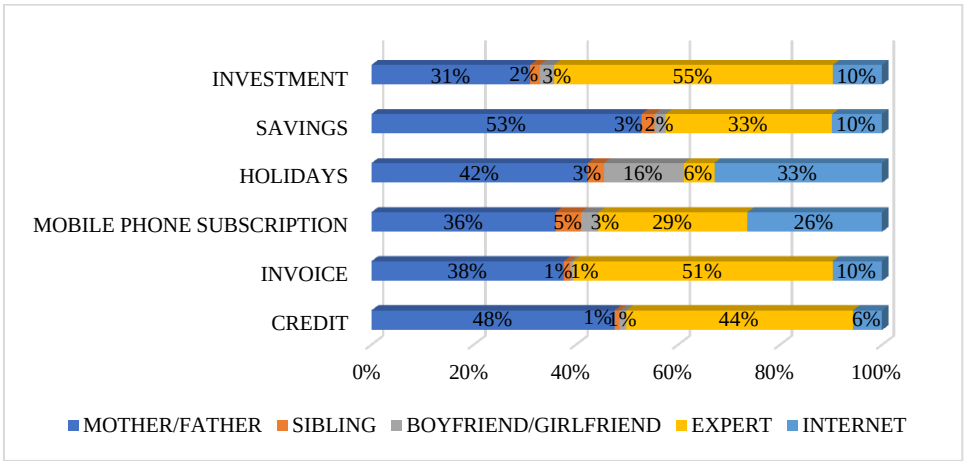

Figure 3. Primary information sources in financial decision-making situations, Source: Own work

Fig. 3 illustrates our research results in relation to primary sources of financial advice; parental advice is the most important so the family is the prime information resource. Another crucial information source is also from financial experts (bankers) and finally online resources. In addition, friends and acquaintances were a less common source.

4. CONCLUSIONS

We can draw the following conclusions from our research results:

1. The students of the Engineering Faculty are aware of the future, most of them possess savings. There are no gender differences considering savings, because they own savings in a very similar rate. Generally, they keep their money in bank accounts or in cash at home, they do not tend to choose investments as a type of saving solution. Students can be considered as risk-adverse.
2. The debit card use is certainly widespread and frequent, also the majority of the students own at least one personal debit card with weekly use.
3. Most of the respondents do not have a student loan, so in this respect they can also be considered risk-adverse.

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4. Csernák's [4] findings and our numerical results show that the household income is not the strongest influencing factor in the financial decision-making process. We did not find a correlation between their existing savings, loan and monthly income rate. However, it is worth mentioning that previous financial studies have impacted the students' savings related behaviours.
5. The research statements have led to the next conclusions, such as the students are not prioritizing material goods, they do not use money to influence others and they do not associate money with success.
6. In relation to the student's information resources, the results were similar to our previous findings. The majority of the respondents would ask their parents about savings, holiday, mobile subscription and loan related issues. It is worth mentioning that the family is the prime information source of the young adults, communication with their parents is critical.

It would be essential to carry out further research among the students of dual education in order to learn more about the topic [19].

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